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MODERN CONCEPTS OF CLAY MATERIALS[1]

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ABSTRACT

Clay materials are composed essentially of minute crystalline particles of any one or more members of a few groups of minerals known as the "clay minerals." Using this clay-mineral concept as a point of departure, researches starting from the many fields in which clay materials are important—from agriculture, engineering, geology, and the ceramic, rubber, paper, petroleum, and many other industries—have in the last fifteen years made outstanding progress toward a more satisfactory and complete understanding of the precise composition of clay materials, their structure, and the factors that determine their properties.

The occurrence of the various clay minerals in soils, contemporaneous sediments, and ancient clays and shales is summarized briefly, and general conclusions are drawn that seem warranted. Pertinent information on the composition, structure, and certain properties of the individual clay minerals is assembled. Finally, the structural relationships of clay-mineral particles and water are analyzed for clay materials in the plastic state, and some new interpretations are suggested.

INTRODUCTION

Clay materials are important in many fields of human endeavor: in agriculture, because they make up an essential part of soils; in construction engineering, because structures are built on them and with them; and in the ceramic, rubber, paper, petroleum, metal-founding, and many other industries, because they are an important raw material. Research workers in all these fields have always been intensely interested in clay materials, and a great fund of information regarding them has gradually accumulated.

[1] Address delivered at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941. Published by permission of the chief, Illinois State Geological Survey.

About fifteen years ago new research tools became available for the investigation of clay materials that opened new fields for fundamental study. As a consequence, new interest was aroused in clay problems, and clay-research activities began an expansion that is still continuing. Mineralogists, physicists, chemists, and engineers from various fields began fundamental studies that have made outstanding progress toward a more satisfactory and complete understanding of the composition, occurrence, and properties of clay materials. This recent work has shown for the first time the character of the mineralogical units that make up clay materials, including their finest size grades. Also, and of great importance, it has shown the lattice structures of these individual units that are the building-blocks of clay materials. An outgrowth of this work has been the so-called "clay-mineral concept" of the composition of clay materials.

Along with the studies of the precise composition of clays has come a tremendous amount of work on the properties of the individual clay minerals, and this work has led to a real insight into the cause of the properties of clay materials and the factors that determine them. In addition, work on the origin and distribution of the clay minerals promises to permit a more satisfactory unraveling of the geologic record locked up in argillaceous sediments.

DEFINITIONS

Although everyone knows what is meant by the term "clay," a precise definition is not easy to formulate. Recently quite satisfactory definitions have been published by the Committee on Sedimentation of the National Research Council[2] and by a committee of the American Ceramic Society,[3] following independent study of present and past usage of this term.

The term "clay" as used today carries with it three implications: (1) a natural material with plastic properties, (2) an essential composition of particles of very fine size grades, and (3) an essential composition of crystalline fragments of minerals that are essentially hydrous aluminum silicates or occasionally hydrous magnesium

[2] W. H. Twenhofel, "Terminology of Fine-grained Mechanical Sediments," *Nat. Res. Coun. Rept. Com. on Sed. 1936–37* (1937), pp. 81–104.

[3] "American Ceramic Society Committee Report," *Bull. Amer. Ceramic Soc.*, Vol. XVIII (1939), pp. 213–15.

silicates. The term implies nothing regarding origin but is based on properties, texture, and composition, which are, of course, interrelated—for example, the plastic properties are the result of the constituent minerals and their small grain size.

"Shale" is the term used generally[4] to designate material that differs from clay only in being laminated and slightly more indurated.

"Clay material" is used in this report to designate any natural material having the three attributes listed previously. It includes, therefore, such material as clay, shales, soils (of the agriculturist), etc. The term "clay material" is preferred as a general term rather than "clay," because the truth is that in many fields some such materials are not thought of as falling under the classification of clay. The term is not used here to include materials composed primarily of bauxitic or limonitic material. These materials may be fine grained, but they do not possess those attributes of composition or properties required by the term "clay."

CONCEPTS OF THE COMPOSITION OF CLAY MATERIALS

Many concepts of the composition of clay materials have been suggested. For a consideration of them the works of J. M. van Bemmeln,[5] H. Stremme,[6] H. E. Ashley,[7] G. Caslow,[8] E. Dittler,[9] H. Salmang,[10] S. Mattson,[11] S. J. Thugutt,[12] J. Lemberg,[13] and R. Gans[14] should be consulted.

[4] Twenhofel, *op. cit.*

[5] "Contribution to the Knowledge of Silicate Disintegration Products in Clayey, Volcanic, and Lateritic Soils," *Zeitschr. anorg. Chem.*, Vol. XLII (1904), pp. 265–314.

[6] "The Chemistry of Kaolins," *Fortschr. Min. Krist. u. Petrog.*, Vol. II (1912).

[7] "Colloid Matter of Clay and Its Measurement," *U.S. Geol. Surv. Bull. 388* (1909), p. 62.

[8] "Relations between Kaolin and Clay," *Chem. d. Erde*, Vol. II (1926), pp. 415–41.

[9] "Chemic-genetic Problems of Clay and Kaolin Research," *Tonindustrie-Zeitung*, Vol. LVI (1932), pp. 836–38, 891–93, 939–40.

[10] *Ceramics* (Berlin, 1933).

[11] "Chemical Characteristics of Soil Profiles," *Lantbrukshogskolans, Annales 2* (Stockholm, Sweden, 1935).

[12] "Are Allophane, Halloysite, Montmorillonite Units or Are They Mixtures of Alumina and Silica Gels," *Centralblatt f. Min.*, 1911, pp. 97–103.

[13] "On the Alteration of Silicates," *Zeitschr. deutsch. geol. Gesellsch.*, Vol. XXVIII (1876), pp. 519–672; "On the Rock Alteration at Predazzo and Monzoni," *ibid.*, Vol. XXIX (1877), pp. 457–511.

[14] "Zeolites and Similar Compounds, Their Constitution and Significance," *Jahrb. kgl. preusz. geol. Landesandst*, Vol. XXVI (1906), p. 179.

With the development of X-ray diffraction analysis a research tool became available for determining the makeup of the finest fraction of clay materials. A. Hadding,[15] in 1923, and F. Rinne,[16] in 1924, were the first to apply this tool to clays. It soon became evident that clays were composed almost entirely of crystalline material and that the properties of clays would have to be explained on the basis of definite crystalline compounds. X-ray researches, materially aided by precise and painstaking optical work by C. S. Ross[17] and others,[18] soon revealed the specific mineral identity of the components of clay materials. As a result of this work the present widely accepted concept of the clay-mineral composition of clay materials was developed.

CLAY-MINERAL CONCEPT

Extensive research[19] in many laboratories has shown, beyond reasonable doubt, that clay materials are composed essentially of crystalline particles of members of any one or more of a few groups of minerals known as the "clay minerals." The clay minerals are hydrous aluminum silicates, frequently with some replacement of the aluminum by iron and magnesium and with small amounts of alkalies and alkali-earths. In rare instances magnesium and iron completely replace the aluminum. In addition to the clay minerals, variable but usually small amounts of quartz, limonitic material,

[15] "An X-ray Method to Identify Crystalline and Cryptocrystalline Substances," *Zeitschr. Krist.*, Vol. LVIII (1923), pp. 108–12.

[16] "X-ray Investigation of Finely Divided Minerals, Manufactured Products and Dense Rocks," *Zeitschr. Krist.*, Vol. LX (1924), pp. 55–69.

[17] "The Mineralogy of Clays," *1st Internat. Cong. Soil Sci.*, Vol. V (1928), pp. 555–56.

[18] C. E. Marshall, "The Orientation of Anisotropic Particles in an Electrical Field," *Trans. Faraday Soc.*, Vol. XXVI (1930), pp. 173–89; R. E. Grim, "Petrography of the Fuller's Earth Deposit, Olmsted, Illinois, with a Brief Study of Some Non-Illinois Earths," *Econ. Geol.*, Vol. XXVIII (1933), pp. 345–63.

[19] S. B. Hendricks and W. H. Frey, "The Results of X-ray and Microscopic Examinations of Soil Colloids," *Soil Sci.*, Vol. XXIX (1930), pp. 457–78; W. P. Kelley, W. H. Dore, and S. M. Brown, "The Nature of the Base-Exchange Material of Bentonite, Soils, and Zeolites as Revealed by Chemical Investigations and X-ray Analysis," *Soil. Sci.*, Vol. XXXI (1931), pp. 25–45; Grim, *op. cit.;* K. Endell, U. Hofmann, and D. Wilm, "The Nature of Ceramic Clays," *Ber. deutsch. keram. Gesellsch.*, Vol. XIV (1933), pp. 407–38; C. W. Correns, "On the Constituents of Clay," *Zeitschr. deutsch. geol. Gesellsch.*, Vol. LXXXV (1933), pp. 706–11; Marshall, "Mineralogical Methods for the Study of Silts and Clays," *Zeitschr. Krist.*, Vol. XC (1935), pp. 8–34.

boehmite, hydrargillite,[20] and organic material may be present. Feldspar, pyrite, and a host of other minerals may be present as extremely minor constituents or as prominent constituents in occasional clays. Except for a few clay minerals—for example, attapulgite—that are fibrous,[21] all the clay minerals occur in flat flake-shaped particles. (See discussion of the structures of the clay minerals.)

The clay minerals occur in most clay materials in particles less than about 5 μ (0.005 mm.) in diameter. They possess excellent cleavages; and, when mixed with water, the particles are frequently reduced in size,[22] so that a wet determination of the particle-size distribution will usually show most of the clay minerals in particles less than 0.002 mm. even though they are coarser in the crude state. Recent studies with the electron microscope[23] have indicated that certain of the clay minerals can exist in particles approaching their unit cell height, that is about 1 mμ. Organic materials may be present in particles less than 0.1 μ in diameter, and the particles of hydroxides of aluminum and ferric iron may be at least as small as 1 μ. Silica in the form of quartz is known[24] in clay materials as small as 0.1 μ, and perhaps in even smaller size grades in the form of cristobalite.[25]

The clay minerals, except allophane,[26] are crystalline; and much

[20] Mehmel, "X-ray Data for Mineral Determinations," *Fortschr. Min. Krist. u. Petrog.*, Vol. XXIII (1939), pp. 91–118.

[21] W. F. Bradley, "The Structural Scheme of Attapulgite," *Amer. Min.*, Vol. XXV (1940), pp. 405–10; G. Nagelschmidt, "Rod-shaped Clay Particles," *Nature*, Vol. CXLII (1938), pp. 114–15.

[22] Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceramic Soc.*, Vol. XXII (1939), pp. 141–51.

[23] M. Ardenne, K. Endell, and U. Hofmann, "Investigation of the Finest Fractions of Bentonite and Clay Soils with the Universal Electron Microscope," *Ber. deutsch. keram. Gesellsch.*, Vol. XXI (1940), pp. 209–27.

[24] Grim and R. H. Bray, "The Mineral Constitution of Various Ceramic Clays," *Jour. Amer. Ceramic. Soc.*, Vol. XIX (1936), pp. 307–15.

[25] A. von Moos, "Unconsolidated Sediments and Soil Mechanics," *Geol. Rund.*, Vol. XXIX (1938), pp. 368–81; Marshall, "Layer Lattices and the Base-Exchange Clays," *Zeitschr. Krist.*, Vol. XCI (1935), pp. 433–49.

[26] C. S. Ross and P. F. Kerr, "Halloysite and Allophane," *U.S. Geol. Surv. Prof. Paper 185-G* (1935).

research[27] indicates that almost all clays, including their smallest constituent particles, are made up entirely of crystalline material. Some clay materials[28] do contain a small amount of amorphous inorganic substance, but it is an extraneous material. The crystalline clay minerals are the dominant components of clay materials, and their properties must be accounted for on the basis of the crystalline components.

FACTORS CONTROLLING THE PROPERTIES OF CLAYS

Following are the factors which are necessary to characterize completely a clay material. These are also the general factors that determine what the properties of a given clay material will be.

1. Clay-mineral composition—the relative abundance of the clay-mineral components and their particle-size distribution.
2. Nonclay-mineral composition—the relative abundance of each mineral and the size-grade distribution of its particles.
3. Electrolyte content—quantitative determinations of the individual exchangeable bases and any water-soluble salts.
4. Organic content—the amount and kind.
5. Miscellaneous textural characteristics[29] such as shape of quartz grains, degree of parallel orientation of the clay-mineral particles, silicification, etc.

Ultimate chemical composition has been omitted from the list of factors controlling properties because it is the units (i.e., minerals) in which the silica, alumina, etc., are combined, rather than their total amounts, that are important. However, if one is interested in a single property, particularly a fired property such as burning color, an ultimate analysis may be of value. It is generally true that a chemical analysis alone, without X-ray, optical, and other mineralogical data, tells very little about the properties of a clay material and, in fact, the analysis may be completely misleading.[30]

[27] Endell *et al.*, *op. cit.;* Grim and Bray, *op. cit.;* K. Jasmund, "Mineral Content of Kaolin with Special Consideration of Colloidal Size Ranges," *Chem. d. Erde.*, Vol. XII (1940), pp. 508–35.

[28] Grim, *op. cit.;* Ross and Kerr, *op. cit.;* Correns, *op. cit.;* H. J. Hellmers and R. Kohlers, "The Determination of Alumina and Silica Gel in Soils by Optical Methods," *Mitt. preuss. geol. Landesanst.*, Vol. XXI (1935).

[29] Grim, "Petrographic and Ceramic Properties of the Pennsylvanian Shales of Illinois," *Jour. Amer. Ceramic Soc.*, Vol. XXIV (1941), pp. 23–28.

[30] Mehmel, "New Methods for the Study of Clays," *Zement, H. 4–6* (1939), 15 pp.; Marshall, "The Chemical Composition and Crystal Structure of the Clay Minerals," *3d Internat. Cong. Soil Sci.*, Vol. III (1936), pp. 95–97.

No mention is made of pH for the reason that the character and relative amount of the ions that determine the pH are important rather than the pH itself.[31] Similarly, no mention is made of base-exchange capacity because that depends on the character of the clay mineral, and for certain clay minerals (see later discussion of base exchange) also on particle size.

CLAY MINERALS—CLASSIFICATION AND COMPOSITION

The clay minerals are the primary constituents of clay materials, and they are the most important single factor in determining the properties of these materials.

GROUPS OF MAJOR IMPORTANCE

Illite group.—The name "illite" was suggested by Grim, Bray, and Bradley[32] as a group name rather than as a specific mineral name for the constituents of clay materials that are similar to, but not identical to, the white micas. Illites contain less potash and more water than the white micas and also differ from them in certain physical properties. The presence of such constituents in clays had been recognized before, and the names "mica-like clay mineral,"[33] "sericite-like mineral,"[34] and "potash-bearing clay mineral"[35] had been applied. These names were confusing, and, as available data suggested that such constituents should be placed together in a single group, a name for the group became desirable.

Grim and others[36] advanced the general formula $(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)Si_{8-y} \cdot Al_yO_{20}$ with y varying from 1 to 1.5. This

[31] Endell and P. Vageler, "The Cation and Water Hull of Ceramic Clays in the Unfired State," *Ber. deutsch. keram. Gesellsch.*, Vol. XIII (1932), pp. 377–411; R. C. Spivey, "Bentonite in Southwestern South Dakota," *Rept. Invest. 36, So. Dakota Geol. Surv.* (1940).

[32] Grim, Bray, and Bradley, "The Mica in Argillaceous Sediments," *Amer. Min.*, Vol. XXII (1937), pp. 813–29.

[33] Endell, Hofmann, and Maegdefrau, "The Nature of Clay Used as Raw Material in the German Cement Industry," *Zement*, Vol. XXIV (1935), pp. 625–32; Maegdefrau and Hofmann, "The Mica Clay Mineral," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp. 31–59.

[34] Grim, "Petrology of the Pennsylvanian Shales and Non-calcareous Underclays of Illinois," *Bull. Amer. Ceramic Soc.*, Vol. XIV (1935), pp. 113–19, 129–34, 170–76.

[35] Ross and Kerr, "The Clay Minerals and Their Identity," *Jour. Sed. Pet.*, Vol. I (1931), pp. 55–65.

[36] Grim, Bray, and Bradley, *op. cit.*

formula indicates that illites may be heptaphyllitic and octophyllitic, which is contrary to A. N. Winchell's[37] finding of "no evidence of crystal solubility between octophyllite and heptaphyllite micas." Recent work by S. B. Hendricks and M. E. Jefferson[38] has tended to support the division of the micas into the two groups suggested by Winchell. Muscovite is heptaphyllitic and so has only two-thirds of the possible positions in the alumina sheet occupied, whereas biotite is octophyllitic and so has all the possible positions filled. (See discussion of structure.) Maegdefrau and Hofmann[39] have shown that illite (the mica-clay mineral) is structurally like muscovite rather than biotite. Most illites that have been analyzed are definite heptaphyllites, but a few contain an excess of iron and/or magnesium. Whether this excess is due to a failure to purify completely the sample or to an actual mixing of types remains to be decided by further work.

Illites are known which contain almost no iron,[40] but most of them contain some replacement of aluminum by iron and magnesium. The upper limit of aluminum replacement is not known. According to Maegdefrau and Hofmann[41] and Hendricks and L. T. Alexander,[42] glauconite is closely similar in structure to the illites.

Montmorillonite group.—This group takes its name from the mineral montmorillonite, with a probable composition of $(OH)_4Al_4Si_8O_{20} \cdot xH_2O$.[43] The aluminum is usually partly replaced by magnesium and ferric iron. In some cases the substitution is essentially complete, and then the names "saponite" and "nontronite" are applied, respectively. All the members of this group have an expanding lattice (see discussion of structure of the clay minerals), and this has come to be the diagnostic criterion for this group. Beidellite has been placed in this group and defined as differing from montmorillonite by having a molecular silicate-to-alumina ratio of 3:1 instead

[37] "Studies in the Mica Group," *Amer. Jour. Sci.*, ser. 5, Vol. IX (1925), pp. 309–27, 415–30.

[38] "Polymorphism of the Micas," *Amer. Min.*, Vol. XXIV (1939), pp. 729–71.

[39] *Op. cit.* [40] *Ibid.* [41] *Ibid.*

[42] "Minerals Present in Soil Colloids," *Soil Sci.*, Vol. XLVIII (1939), pp. 257–71.

[43] U. Hofmann, K. Endell, and D. Wilm, "Crystal Structure and Swelling of Montmorillonite," *Zeitschr. Krist.*, Vol. LXXXVI (1933), pp. 340–48.

of 4:1.[44] Unpublished work by the writer and his colleagues indicates that some so-called "beidellite" is a mixture of montmorillonite and limonite and that some others have a nonexpanding lattice which, together with other properties, suggests that they are clay-mineral mixtures containing large amounts of illite. The validity of the species is, therefore, open to question.

Kaolinite group.—Kaolinite, the chief member of this group, has the composition $(OH)_8Al_4Si_4O_{10}$.[45] Dickite and nacrite, with the same composition but slightly different crystallographic forms, are very rare constituents of argillaceous sediments. Anauxite, like kaolinite except for a higher silica-to-alumina molecular ratio, is also a member of this group. Only a few occurrences of anauxite have been reported.[46]

Constituents of clays have been reported that could be interpreted as kaolinite in which the aluminum has been replaced by ferric iron;[47] however, stronger evidence favors the conclusion that such substitution does not actually exist. Hendricks[48] has recently pointed out structural reasons for the absence of substitutions in the kaolinite lattice.

GROUPS OF MINOR IMPORTANCE

Halloysite.—Hofmann, Endell, and Wilm[49] stated that halloysite with the composition $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ ($[OH]_{16} \cdot Al_4 \cdot Si_4 \cdot O_6$) loses $2H_2O$ on heating to about 50° C. and changes over to kaolinite. Mehmel[50] has confirmed the change of 50° C. but has shown that the

[44] Ross and Kerr, *op. cit.*

[45] Ross and Kerr, "The Kaolin Minerals," *U.S. Geol. Surv. Prof. Paper 165-E* (1931).

[46] V. T. Allen, "Eocene Anauxite Clays and Sands in the Coast Range of California," *Bull. Geol. Soc. Amer.*, Vol. LII (1941), pp. 271–94.

[47] J. S. Hosking, "The Soil Clay Mineralogy of Some Australian Soils Developed on Basaltic and Granitic Parent Material," *Jour. Coun. Sci. and Ind. Res.*, Vol. XIII (1941), pp. 206–11.

[48] "Random Structures of Layer Minerals as Illustrated by Cronstedite ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$). Possible Iron Content of Kaolinite," *Amer. Min.*, Vol. XXIV (1939), pp. 529–39.

[49] "X-ray and Colloid Chemical Study of Clays," *Zeitschr. angewandte Chemie*, Vol. XLVII (1934), pp. 539–47.

[50] "On the Structure of Halloysite and Metahalloysite," *Zeitschr. Krist.*, Vol. XC (1935), pp. 35–43.

mineral resulting after the loss of $2H_2O$ is not kaolinite. Accordingly, there are two forms of halloysite, which Mehmel designates as "halloysite," $(OH)_{16}Al_4 \cdot Si_4O_6$, and "metahalloysite," $(OH)_8Al_4Si_4O_{10}$, the latter being the higher temperature form. Hendricks[51] has suggested the names "hydrated halloysite" and "halloysite," respectively, for these minerals, thus retaining the name "halloysite" for material of the composition to which it was first applied. In recent work C. H. Edelman and J. Ch. L. Favejee[52] have followed the usage of Mehmel because "the name 'hydrated halloysite' for the mineral rich in water gives the erroneous impression that this substance originates from the mineral poor in water." Actually, the higher hydrated form has not been prepared from the lower hydrated form in the laboratory. No substitutions within the lattice of the halloysite minerals have been reported.

Attapulgite.[53]—The name "attapulgite" was suggested by J. de Lapparent[54] for the unique clay mineral composing certain Georgia and Florida fuller's earths and clays at Mormoiron, France. Recent work of Bradley[55] tends to confirm the species, and he suggests the formula $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ in which there is some replacement of Mg by Al. De Lapparent[56] gives $Si_3O_{12}(Al_{4/3} \cdot Mg_2)H_8$ as the formula for the mineral.

Allophane.—Ross and Kerr[57] suggest that the term "allophane" be used to include all noncrystalline mutual solutions of silica, alumina, and water in varying amounts. Minor amounts of bases may also be present. The term "allophane" would then be applicable to the small amount of amorphous material found occasionally in some clays.

[51] "On the Structure of the Clay Minerals, Dickite, Halloysite, and Hydrated Halloysite," *Amer. Min.*, Vol. XXIII (1938), pp. 275–301.

[52] "On the Crystal Structure of Montmorillonite and Halloysite," *Zeitschr. Krist.*, Vol. CII (1940), pp. 417–31.

[53] Unfortunately not named "Floridin," since the fuller's earth that contains it in Georgia and Florida was known first by that name.

[54] "An Essential Constituent of Fuller's Earth," *Compt. rend. Acad. sci.*, Vol. CCI (1935), pp. 481–83.

[55] "The Structural Scheme of Attapulgite," *Amer. Min.*, Vol. XXV (1940), pp. 405–10.

[56] "Formula and Structural Scheme of Attapulgite," *Compt. rend. Acad. sci.*, Vol. CCII (1936), pp. 1728–31.

[57] *Op. cit.*

The term "allophane" or "allophaneton"[58] has been used widely in Europe, particularly by ceramists, to designate the portion of a clay that is soluble in hydrochloric acid. Allophane (usage of Ross and Kerr) and the montmorillonite minerals are more acid-soluble than the other clay minerals, but the use of allophane based on acid solubility has no mineralogical significance,[59] chiefly because the effect of variations in particle size is ignored.

Chloritic mica.—Microscopic study of clays and shales composed largely of illite frequently shows green flaky masses of material that have the optical properties of chloritic micas. X-ray diffraction analyses of the finer fractions of such rocks also indicate the presence of crystalline material with the general characteristics of chloritic mica. It has not yet been possible to isolate this material so that it could be studied in detail and definitely classified.

QUESTIONABLE CLAY MINERALS

Fersman[60] suggested the existence of a series of minerals between paramontmorillonite and parasepiolite which he called "palygorskites." Paramontmorillonite and parasepiolite were considered to be acicular forms of montmorillonite and sepiolite. The xylotile group was considered to contain the iron analogues of the palygorskites. According to De Lapparent,[61] thermal analyses indicate that palygorskites are mixtures of kaolinite and sepiolite. H. Longchambon[62] and P. Urbain[63] have also discussed the palygorskites.

According to Ross and Kerr,[64] the type "leverrierite" is composed

[58] H. Stremme, "The Clay Minerals," *Sprechsaal*, Vol. XLVII (1914); Thugutt, *op. cit.*

[59] H. S. Washington, "The Calculation of the 'Rational Analysis' of Clays," *Jour. Amer. Ceramic Soc.*, Vol. I (1918), pp. 405–21; J. S. McDowell, "Rational Analysis of Clay," *Jour. Amer. Ceramic Soc.*, Vol. XIX (1926), pp. 61–65.

[60] A. Fersman, "On the Palygorskite Group," *Bull. Acad. Imp. Sci. St. Petersburg*, Vol. II (1908), pp. 255–74.

[61] "The Place of Montmorillonite in the Group of Phyllite Silicates," *Compt. rend. Acad. sci.*, Vol. CCI (1935), pp. 527–29.

[62] "Characteristics of Palygorskites," *Compt. rend. Acad. sci.*, Vol. CCIV (1937), pp. 55–58.

[63] "Classification of Hydrated Aluminum Silicates," *Compt. rend. Soc. geol. de France*, 1936, pp. 147–49.

[64] *Op. cit.*

of kaolinite, whereas, according to De Lapparent,[65] the name refers to a mixture of white mica and kaolinite. In any event, the term does not designate a single species and should be abandoned.

Kerr[66] has shown that the type "smectite" is composed of montmorillonite. Faratsihite, according to Hendricks,[67] is a mixture of nontronite and kaolinite.

The exact status of other suggested species, such as monothermite,[68] keffekillite,[69] gedroizite,[70] bravaisite, elbrussite,[71] ablykite,[72] and donbassite,[73] remains for future work to decide.

It should not be assumed that all valid species of clay minerals have been described. Particularly in the case of the magnesium-clay minerals, it seems possible that other species will be found. There are some clays, such as the bentonite from Tehachapi, California, that contain appreciable magnesium (8 per cent $\pm$MgO),[74] and their properties do not seem to fit exactly with described species. W. von Englehardt,[75] De Lapparent,[76] and D. P. Serdyuchenko[77]

[65] "Constitution and Origin of Leverrierite," *Compt. rend. Acad. sci.*, Vol. CXCVIII (1934), pp. 669–71.

[66] "Montmorillonite or Smectite as Constituents of Fuller's Earth and Bentonite," *Amer. Min.*, Vol. XVII (1932), pp. 192–97.

[67] "Random Structures . . . . ," *op. cit.*

[68] D. S. Beliankin, "On the Characteristics of the Mineral 'Monothermite,'" *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XVIII (1938), pp. 673–76.

[69] Anonymous, "Deposits of 'Kel'-like Clays in the Tertiary Formations of the Crimea," *United Geol. and Prosp. Serv. U.S.S.R. Bull. 50* (1930), pp. 1131–40.

[70] I. D. Sedletsky, "Gedroizite in the Alkali-Soils," *Compt rend. Acad. sci. U.S.S.R.*, Vol. XXIII (1939), pp. 565–68.

[71] I. J. Mickey, "On a New Mineral of the Nontronite-Beidellite Group," *Centralblatt f. Min.*, Vol. A (1930), pp. 293–303.

[72] Sedletsky and S. Yusupova, "Argillaceous Minerals Closely Approaching Halloysite," *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XXVI (1940), pp. 944–47.

[73] E. K. Lazarenko, "Donbassites, a New Group of Minerals from the Donetz Basin," *Compt. rend. Acad. sci. (Doklady) U.S.S.R.*, Vol. XXVIII (1940), pp. 509–21.

[74] Kerr and E. M. Cameron, "Fuller's Earth of Bentonite Origin from Tehachapi, California," *Amer. Min.*, Vol. XXI (1936), pp. 230–37.

[75] "The Silicate Clay Minerals," *Fortschr. Min. Krist. u. Petrog.*, Vol. XXI (1937), pp. 276–337.

[76] "Formulae, Structures, and Classification of Clays," *Zeitschr. Krist.*, Vol. XCVIII (1938), pp. 233–58.

[77] "About the Constitution and Nomenclature of Some Water Aluminum Silicates," *17th Internat. Geol. Cong. Spec. Pub. No. 10* (1937).

have recently discussed in detail the problems of these magnesium-clay minerals.

INTERSTRATIFIED CLAY MINERALS

Recent investigations have shown that when several clay-mineral species are present in a clay material they are often closely intergrown. The intergrowth is essentially an interstratification of basal cleavage plates of the different clay minerals. Hendricks and Alexander[78] have indicated an interstratification of montmorillonite and illite in the colloid fractions of certain soils, and Bray[79] has made the same suggestion for some Illinois soils. Hendricks[80] has shown that faratsihite is an intergrowth of kaolinite and nontronite, and De Lapparent[81] uses the term "leverrierite" to indicate a mixture of white mica and kaolinite.

Unpublished work by the author and Bradley has checked the conclusions of Hendricks and Bray for soil colloids. The general character of the optical properties of such intergrowths in some soils would seem to require a regular, rather than a random, intergrowing with the units of the different clay minerals of the order of height of about one unit cell. It has been observed frequently that many shales containing kaolinite, chloritic micas, and illite probably represent less-intimate intergrowth than in the soil colloids.

The existence of such intergrowths vastly complicates the complete identification of all the clay minerals in a given clay material. Frequently the use of a single criterion for identification of the constituent minerals will not reveal all the components of the interstratification. Only a combination of optical, X-ray, chemical, and thermal data will provide the complete picture.

CLAY MINERALS—STRUCTURE

Since the application of X-ray diffraction analysis to clay minerals, a vast body of data has accumulated on the lattice structure of these minerals. The details of some of these structures are still a matter of some controversy, but the broader features based on gen-

[78] *Op. cit.*

[79] "Chemical and Physical Changes in Soil Colloids with Advancing Development in Illinois Soils," *Soil Sci.*, Vol. XLIII (1937), pp. 1–14.

[80] "Random Structures . . . . ," *op. cit.*

[81] "Constitution and Origin . . . . ," *op. cit.*, pp. 669–710.

eralizations of L. Pauling[82] seem to be reasonably well established. For the details of the individual structures the cited references should be consulted.

Two structural units are involved in the atomic lattices of the clay minerals. One is the alumina or aluminum hydroxide unit, which consists of two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls. Actually, only two-thirds of the possible aluminum positions are occupied in this unit, which is the gibbsite structure. The mineral brucite possesses a similar structure except that all possible aluminum positions are occupied by magnesium. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valences being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom such that that silicon valency is analogous to the common hydroxyl group of gibbsite.

Montmorillonite.—The montmorillonite structure suggested by Hofmann, Endell, and Wilm[83] consists of structural units of one gibbsite sheet between two sheets of silica tetrahedral groups (Fig. 1). The structural units are stacked one above the other in the direction of the *c*-axis and, according to Maegdefrau and Hofmann,[84] without orientation in the *a* and *b* directions. Hendricks and Ross,[85] however, on the basis of optical and diffraction data, indicate some orientation in the *a* and *b* directions.

The units are loosely held together in the direction of the *c*-axis

[82] "The Structure of Micas and Related Minerals," *Proc. Nat. Acad. Sci.*, Vol. XVI (1930), pp. 123–29.

[83] *Op. cit.*

[84] "The Crystal Structure of Montmorillonite," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp. 299–323.

[85] "Lattice Limitations of Montmorillonite," *Zeitschr. Krist.*, Vol. C (1938), pp. 251–64.

with water present between them. The amount of water between the units varies, and there is a correlated variation in the *c*-dimension, so that the mineral is said to have an expanding lattice. Without water between the structural units the lattice is like that of pyrophyllite except that the height of the cell is 9.6 A, as against 9.2 A for pyrophyllite. The increased height of the montmorillonite cell is explained[86] by the presence of cations between the units. In the absence of water the distance between the units measured from the

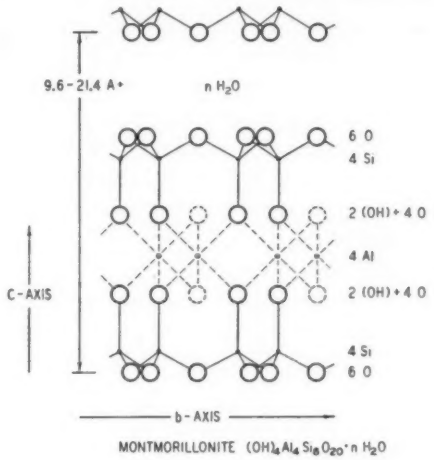

FIG. 1.—Schematic presentation of the structure of montmorillonite. (After Hofmann, Endell, and Wilm.)

centers of oxygens is 3.0 A. According to Hofmann and J. Endell,[87] the maximum recorded expansion has given a *c*-dimension of 30 A. Maegdefrau and Hofmann[88] state that the mineral is orthorhombic, whereas Gruner[89] believes it to be monoclinic.

Replacement of Al^{+++} gibbsite positions by Mg^{++} and Fe^{+++} lead

[86] "The Relation of Cation Exchange and Swelling of Montmorillonite to Preheating," *Zeitschr. verien. deutsch. Chem.*, Vol. XXXV (1939).

[87] *Ibid.*

[88] "The Crystal Structure . . . . ," *op. cit.*

[89] "The Structural Relationships of Nontronite and Montmorillonite," *Amer. Min.*, Vol. XX (1935), pp. 475–83.

to saponite and nontronite, respectively. It has been suggested[90] that Si^{++++} may be replaced by Al^{+++}, and Marshall[91] believes that beidellite is the member of the montmorillonite group in which such replacement has been appreciable. G. Nagelschmidt[92] believes that about 1 out of 6 Si^{++++} may be replaceable by Al^{+++}. Substitution of Al^{+++} for Si^{++++} to a marked degree leads to the nonexpanding muscovite structure and therefore appears unlikely,[93] unless it is assumed that the charges resulting from the substitution are balanced in the alumina sheet.[94]

A striking property of the montmorillonite lattice is that aluminum can be removed by acid leaching until there is only 1.7 Al to 4 Si before the lattice structure is destroyed.[95] The aluminum is removed first to exchange positions before going into solution. Leaching with salt solution also removes some aluminum from the lattice.[96]

The amount of the expansion of the montmorillonite lattice is related to the character of the exchangeable base carried by the mineral.[97] For example, Hofmann and K. Giese[98] have suggested that Ca-montmorillonite swells more than NH_4-montmorillonite, and Hofmann and Bilke[99] have shown that montmorillonite with either Na^+, Ca^{++}, or H^+ swells about the same small amount at low vapor pressures but that at higher vapor pressures Na-montmorillo-

[90] Hofmann and W. Bilke, "On the Inner Crystalline Swelling and Base Exchange Capacity of Montmorillonite," *Kolloid Zeitschr.*, Vol. LXXVII (1936), pp. 238–51; Marshall, "Layer Lattices . . . . ," *op. cit.*

[91] Marshall, "Layer Lattices . . . . ," *op. cit.*

[92] "On the Atomic Arrangement and Variability of the Members of the Montmorillonite Group," *Min. Mag.*, Vol. XXV (1938), pp. 140–55.

[93] Grim, "Properties of Clays," *Recent Marine Sediments* (Tulsa, Okla.: Amer. Assoc. Pet. Geol., 1939).

[94] Hofmann and Bilke, *op. cit.*

[95] *Ibid.*

[96] Marshall, "Layer Lattices . . . . ," *op. cit.*

[97] C. W. Davis, H. C. Vacher, and J. E. Conley, "Bentonite, Its Properties, Mining, Preparation and Utilization," *U.S. Bur. of Mines Tech. Paper 609* (1940); H. Freundlich, B. Schmidt, and G. Landau, "The Thixotropy of Bentonite Suspensions," *Kolloid Beihefte*, Vol. XXXVI (1932), pp. 43–81.

[98] "On the Base-Exchange of Clay Minerals," *Kolloid Zeistschr.*, Vol. LXXXVII (1939), pp. 21–36.

[99] Hofmann and Bilke, *op. cit.*

nites swell much more than the others. In general, it appears that Li^+ and Na^+ favor great swelling, whereas Ca^{++}, Mg^{++}, Al^{+++}, H^+, Fe^{+++}, and K^+ tend to reduce it.

The structural unit $Al_4Si_8O_{20}(OH)_4$ suggested by Hofmann and others[100] is a balanced unit and does not explain satisfactorily the swelling in the presence of water, the high base-exchange capacity, and the large adsorption between the basal planes. (See later discussion of base exchange.) Primarily for these reasons, this structural scheme has been questioned by W. Bragg,[101] A. D. Garrison,[102] J. Holzner,[103] De Lapparent,[104] and Edelman and Favejee.[105]

Holzner[106] suggests the formula $Al_{2.3}Si_4O_{10}(OH)_3$ and a structure consisting of a pile of $Al_2(OH)_6$ and a hypothetical unit $Al_{2/3}Si_2O_5$. There appears to be no real basis for such a structure, and it has met with no approval. De Lapparent[107] has suggested a structure that is essentially a combination of pyrophyllite layers and brucite layers $Mg_3(OH)_6$ in which Si has been substituted for 2Mg. This structure has also met with no approval since its thickness is greater than the (001) spacing determined by X-ray analysis.

Recently Edelman and Favejee[108] have suggested a structure that differs from Hofmann's structure[109] in having every other tetrahedron of the silica sheet inverted (Fig. 2) and the substitution of (OH) for the O positions that, as a consequence, would not be balanced. In other words, the silica sheet is considered to have the configuration of cristobalite. According to this scheme, the formula of the silica sheet becomes $O_2Si_4O_6(OH)_2$; of the whole mineral, $(OH)_{12}Al_4Si_8O_{16}\cdot nH_2O$. The mineral should therefore contain $3H_2O$ per Al_2O_3 when $n=0$. It is claimed that this structure more satisfactorily ex-

[100] Hofmann, Endell, and Wilm, *op. cit.*

[101] "Clay," *Royal Inst. Great Britain*, November 19, 1937.

[102] "Surface Chemistry of Clays and Shales," *Amer. Inst. Min. and Met. Engineers, Tech. Pub. 1027* (1938).

[103] "Preliminary Discussion of the Chemical Composition of the Clay Minerals and Corresponding Silicates of Trivalent and Bivalent Metals," *Chem. d. Erde*, Vol. IX (1935), pp. 464–85.

[104] "Formulae, Structures . . . . ," *op. cit.* [105] *Op. cit.* [106] *Op. cit.*

[107] "Formulae, Structures . . . ," *op. cit.*

[108] *Op. cit.* [109] Hofmann, Endell, and Wilm, *op. cit.*

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[90] Hofmann and W. Bilke, "On the Inner Crystalline Swelling and Base Exchange Capacity of Montmorillonite," *Kolloid Zeitschr.*, Vol. LXXVII (1936), pp. 238–51; Marshall, "Layer Lattices . . . . ," *op. cit.*

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[93] Grim, "Properties of Clays," *Recent Marine Sediments* (Tulsa, Okla.: Amer. Assoc. Pet. Geol., 1939).

[94] Hofmann and Bilke, *op. cit.*

[95] *Ibid.*

[96] Marshall, "Layer Lattices . . . . ," *op. cit.*

[97] C. W. Davis, H. C. Vacher, and J. E. Conley, "Bentonite, Its Properties, Mining, Preparation and Utilization," *U.S. Bur. of Mines Tech. Paper 609* (1940); H. Freundlich, B. Schmidt, and G. Landau, "The Thixotropy of Bentonite Suspensions," *Kolloid Beihefte*, Vol. XXXVI (1932), pp. 43–81.

[98] "On the Base-Exchange of Clay Minerals," *Kolloid Zeistschr.*, Vol. LXXXVII (1939), pp. 21–36.

[99] Hofmann and Bilke, *op. cit.*

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[100] Hofmann, Endell, and Wilm, *op. cit.*

[101] "Clay," *Royal Inst. Great Britain*, November 19, 1937.

[102] "Surface Chemistry of Clays and Shales," *Amer. Inst. Min. and Met. Engineers, Tech. Pub. 1027* (1938).

[103] "Preliminary Discussion of the Chemical Composition of the Clay Minerals and Corresponding Silicates of Trivalent and Bivalent Metals," *Chem. d. Erde*, Vol. IX (1935), pp. 464–85.

[104] "Formulae, Structures . . . . ," *op. cit.* [105] *Op. cit.* [106] *Op. cit.*

[107] "Formulae, Structures . . . ," *op. cit.*

[108] *Op. cit.* [109] Hofmann, Endell, and Wilm, *op. cit.*

plains certain physical properties of montmorillonite and the differences between it and pyrophyllite.

W. F. Bradley, R. E. Grim, and G. L. Clark[110] presented evidence to show that the swelling of montmorillonite may take place step-

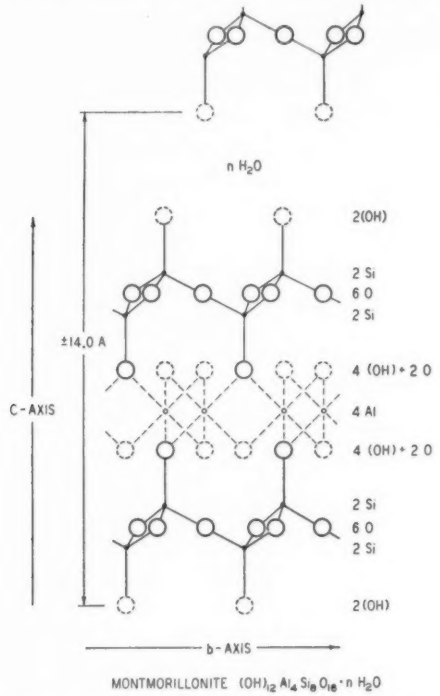

FIG. 2.—Schematic presentation of the structure of montmorillonite. (After Edelman and Favejee.)

wise by the formation of discrete hydrates. According to them, the successive hydrates have *c*-dimensions of 9.6 A, 12.4 A, 15.4 A, 18.4 A, and 21.4 A, corresponding to $2H_2O$, $8H_2O$, $14H_2O$, $20H_2O$, and $26H_2O$. Nagelschmidt[111] has reached a different conclusion. Ac-

[110] "A Study of the Behavior of Montmorillonite upon Wetting," *Zeitschr. Krist.*, Vol. XCVII (1937), pp. 216–22.

[111] "On the Lattice Shrinkage and Structure of Montmorillonite," *Zeitschr. Krist.*, Vol. XCIII (1936), pp. 481–87.

cording to him, as the H_2O increases from 0 to 4 per unit cell, (001) expands from 10.5 A to 15 A; from 4 to 10 H_2O, (001) expands from 15 to 15.9 A; from 10 to 15 H_2O there is no significant expansion; and from 15 to 20 H_2O, (001) expands markedly to 19 A. Maegdefrau and Hofmann[112] conclude that the swelling is continuous. All these workers considered that the water molecules were close packed in the sheets between the basal planes. Very recently Hendricks and others[113] have presented evidence to indicate that the water molecules are not densely packed. (See p. 271 for discussion of configuration of water molecules in the sheets.) According to these workers, the usual situation is that the cleavage spacing varies continuously but not uniformly with the water content. They interpret this as a result of an averaging effect from a lattice that contains various numbers of water layers in different parts. On this interpretation the discrete hydration states referred to above[114] would actually be $2H_2O$, $6H_2O$, $10H_2O$, etc., and these very probably were the states observed.

Illite.—The illite structure is similar to that of montmorillonite suggested by Hofmann and others[115] except that about 15 per cent of the Si^{++++} positions are replaced by Al^{+++}, and the resulting excess charges are satisfied chiefly by K^+ ions between the silica sheets of two successive units[116] (Fig. 3). The K^+ ions appear to act as bridges binding the units together so that they do not expand in the presence of water. The illite structure is similar to the structure of muscovite suggested by Pauling[117] and confirmed by W. Jackson and J. West[118] except that in muscovite one-fourth of the Si^{++++} positions are occupied by Al^{+++} and the number of K^+ is proportionately greater.

In illite Mg^{++} and Fe^{+++} can be substituted for Al^{+++} in the

[112] "The Crystal Structure . . . . ," *op. cit.*

[113] "Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations," *Jour. Amer. Chem. Soc.*, Vol. LXII (1940), pp. 1457–64.

[114] Bradley, Grim, and Clark, *op. cit.*

[115] Hofman, Endell, and Wilm, *op. cit.*

[116] Grim, Bray, and Bradley, *op. cit.*

[117] *Op. cit.*

[118] "The Crystal Structure of Muscovite," *Zeitschr. Krist.*, Vol. LXXVI (1930), pp. 211–27.

octahedral sheet. There appears to be some doubt that Mg^{++} can occupy all the possible positions, that is, substitutions of $3Mg^{++}$ for $2Al^{+++}$, although further work is necessary to settle this point. In other words, illite appears to be heptaphyllitic rather than octophyllitic and to be structurally similar to muscovite rather than to biotite.[119] According to Maegdefrau and Hofmann,[120] the substitution of Mg^{++} for Al^{+++} can be compensated for by substitution of

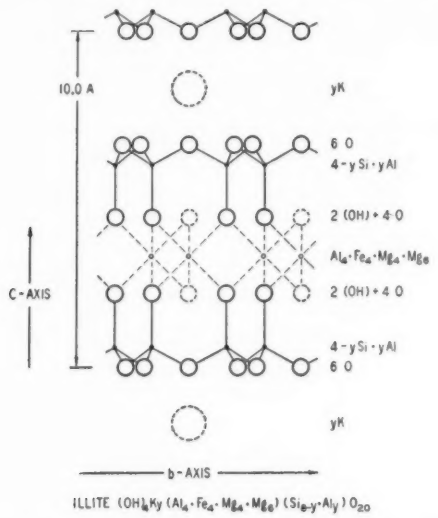

FIG. 3.—Schematic presentation of the crystal structure of illite. (After Grim, Bray, and Bradley.)

(OH) for O, thereby partly explaining the higher water content in illite than in muscovite.

Maegdefrau and Hofmann[121] believe that the diffraction data can be interpreted as an orthorhombic structure, whereas most other workers[122] favor a monoclinic structure. Illite has a pronounced basal cleavage, but it is not so easily cleavable as montmorillonite.

[119] Maegdefrau and Hofmann, "The Mica Clay . . . . ," *op. cit.;* Hendricks and Jefferson, *op. cit.*

[120] Maegdefrau and Hofmann, "The Mica Clay . . . . ," *op. cit.*

[121] *Ibid.*

[122] Hendricks and Jefferson, *op. cit.*

Kaolinite.—The kaolinite structure, as worked out by Gruner,[123] is composed of a gibbsite sheet with a single tetrahedral silica sheet (Fig. 4). The lattice structure does not expand with varying water content, probably because of the attraction of O and (OH) layers which are adjacent when kaolinite units are stacked one above the other. The mineral has basal cleavage but is distinctly less cleavable than montmorillonite. No replacements of the aluminum by iron or magnesium have been proved.

To account for the higher silica-to-alumina molecular ratio of the anauxite member of this group, it was suggested[124] that Si^{++++} replaces Al^{+++}. A recent, more favored suggestion[125] is that some Al^{+++} positions are vacant with corollary changes of O and (OH) to balance the charges on the lattice.

The structures of dickite[126] and nacrite[127] differ from that of kaolinite primarily by a shift or rotation of the layers as they are placed one above the other. According to Gruner,[128] the structure of the kaolinite minerals is monoclinic.

Halloysite.—According to Mehmel,[129] halloysite (hydrated halloysite of Hendricks) is made up of an alternating succession of $Si_2O_3(OH)_2$ and $Al_2(OH)_6$ sheets in the *c*-axis direction (Fig. 5). These sheets are not tied to each other by mutual oxygens. Metahalloysite (halloysite of Hendricks) forms from halloysite by the joining-together of the alumina and silica sheets with the condensation of $2(OH)$ to form H_2O, which escapes, and O, which forms a

[123] "The Crystal Structure of Kaolinite," *Zeitschr. Krist.*, Vol. LXXXIII (1932), pp. 75–88.

[124] *Ibid.*; Gruner, "Densities and Structural Relationships of Kaolinites and Anauxites," *Amer. Min.*, Vol. XXII (1937), pp. 855–60.

[125] Hendricks, "Concerning the Crystal Structure of Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and the Composition of Anauxite," *Zeitschr. Krist.*, Vol. XCV (1936), pp. 245–52.

[126] Gruner, "The Crystal Structure of Dickite," *Zeitschr. Krist.*, Vol. LXXXIII (1932), pp. 394–404.

[127] Gruner, "The Crystal Structure of Nacrite and a Comparison of Certain Optical Properties of the Kaolin Group with Its Structure," *Zeitschr. Krist.*, Vol. LXXXV (1933), pp. 345–54; Hendricks, "The Crystal Structure of Nacrite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and the Polymorphism of the Kaolin Minerals," *Zeitschr. Krist.*, Vol. C (1938), pp. 509–18.

[128] "The Crystal Structure of Nacrite . . . . ," *op. cit.*

[129] "On the Structure of Halloysite . . . . ," *op. cit.*

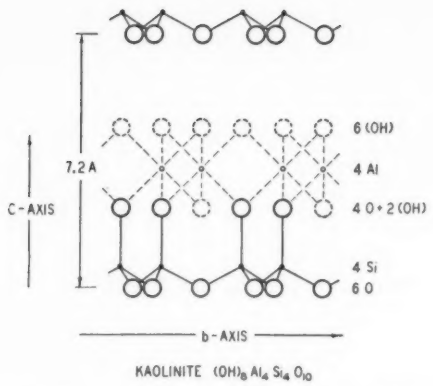

FIG. 4.—Schematic presentation of the crystal structure of kaolinite. (After Gruner)

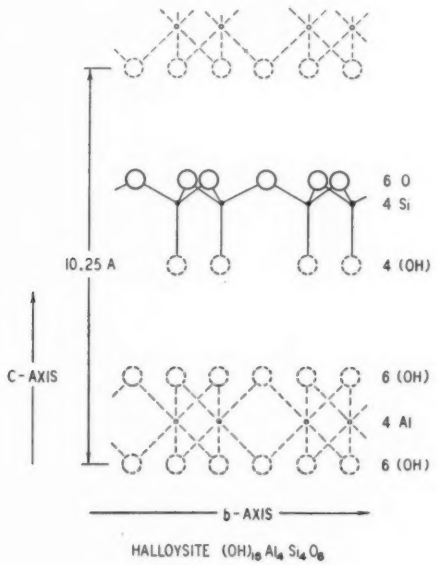

FIG. 5.—Schematic presentation of the crystal structure of halloysite. (After Mehmel.)

bond between the sheets. The resulting structure is closely similar to that of kaolinite.

Hendricks[130] objected to Mehmel's structures because the interaction of the hydroxyl groups would seem to require considerable energy and thus a higher temperature than 50° C. and because the observed intensities of certain reflections are not in accord with expected values. Hendricks[131] suggested that halloysite is composed of neutral ($OH_4Si_2Al_2O_5$) layers interleaved with layers of ($2H_2O$) molecules. Hendricks and M. E. Jefferson[132] explain the limitation of the water molecules to a single layer as due to the O and (OH) sheets of successive layers being adjacent and the resulting partial bonding of the water through (OH) ions.

On the basis of general studies of the properties of the halloysite minerals, P. P. Stout[133] and Edelman and Favejee[134] have suggested other structural arrangements. The former investigator, on the basis of phosphate-fixation experiments, suggested that the halloysite cell consists of two kaolinite layers having their (OH) ion sheets adjacent.

Edelman and Favejee[135] have objected to all the suggested structures on the basis that there is no satisfactory way in which the sheets of the hydrated form are kept together. However, the suggestion of Hendricks and others[136] of an orientation of the water molecules in the sheet (see p. 264) may serve as an explanation. Edelman and Favejee[137] suggest a structure in which every other silica tetrahedron is inverted with substitutions of (OH) for O to balance the charges (Fig. 6). The formula of the unit would be $Al_2(OH)_5OSi_2O_3(OH)$ or $Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$. According to this arrangement, the additional H_2O necessary to fulfil the formula of $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ exists free between the basal sheets. The change to metahalloysite

[130] "On the Structure of the Clay . . . . ," *op. cit.*

[131] *Ibid.*

[132] "Structure of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays," *Amer. Min.*, Vol. XXIII (1933), pp. 863–75.

[133] "Alterations in the Crystal Structure of Clay Minerals as a Result of Phosphate Fixation," *Proc. Soil Sci. Soc. Amer.*, Vol. IV (1939), pp. 177–82.

[134] *Op. cit.*

[135] *Ibid.*

[136] "Structure of Kaolin . . . . ," *op. cit.* [137] *Op. cit.*

takes place by the loss of the H_2O between the basal planes and the action of the (OH) of the silica sheet with an (OH) of the adjacent $Al_2(OH)_6$ sheet of the next unit to form H_2O and a joint O. As evidence for this structure, it is suggested that it explains the similarity of the adsorptive properties of the mineral to those of montmorillonite. It should be pointed out that there is little agreement among students of clay as to the precise character of the adsorptive properties of the halloysite minerals.

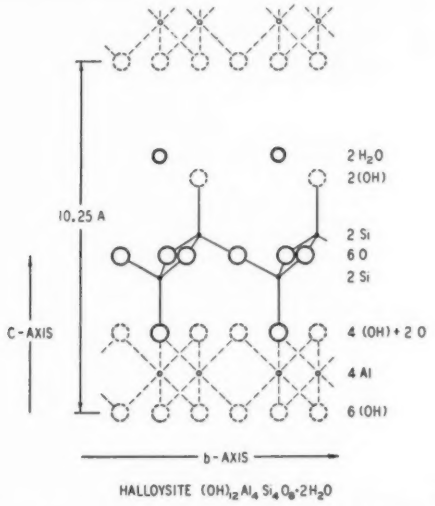

FIG. 6.—Schematic presentation of the crystal structure of halloysite. (After Edelman and Favejee.)

Careful optical work with halloysite shows certain peculiarities difficult to explain on the basis of the suggested structures. If suspensions of halloysite are allowed to dry slowly in a flat-bottomed vessel, so that aggregates are formed,[138] some of them show very perfect interference figures, indicating definite crystal orientation of the units in the aggregate, whereas others appear to be entirely amorphous. All other clay minerals under similar conditions yield aggregates that always show the crystalline character of the min-

[138] Grim, "The Petrographic Study of Clay Minerals—a Laboratory Note," *Jour. Sed. Pet.*, Vol. IV (1934), pp. 45–47.

erals. It would seem from these data that halloysite is composed of units that may easily vary from definite alignment to a random orientation.

Attapulgite.—De Lapparent[139] has suggested that attapulgite is a layer silicate related to the micas. Bradley[140] has shown, however, that the X-ray diagrams obtained for the mineral are "fiber dia-

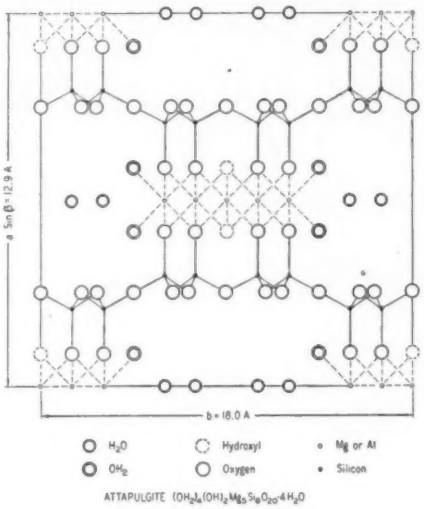

FIG. 7.—Schematic presentation of the crystal structure of attapulgite. (After Bradley.)

grams." The structure suggested by Bradley (Fig. 7) may be described as units of two silica tetrahedra with a brucite sheet between extending indefinitely in only one direction (instead of two directions, as required by sheets) to form ribbons arranged with their long axes parallel to the *c*-axis. The ribbons are joined together through oxygen bonds of the silica sheets so that the silica sheets viewed above are continuous. Chains of water molecules exist in interstices between the ribbons. The composition of the ideal cell is $(OH_2)_4(OH)_2Mg_5Si_8O_{20}\cdot 4H_2O$. Al^{+++} can replace Mg^{++} accom-

[139] "Formula and Structural . . . . ," *op. cit.* [140] *Op. cit.*

panied by vacancies in octahedral positions or may replace Si^{++++} to a limited extent.

Chlorite.—R. E. McMurchy[141] found the structure of six varieties of chlorite of varying composition to be the same. The units of the structure are alternating mica and brucite sheets, with the ideal formula $Al_2Mg_5Si_3O_{10}(OH)_8$. The size of the unit cell varies slightly in different chlorites, and this is explained by replacement of Mg^{++} by Fe^{++}.

CLAY MINERALS—BASE EXCHANGE[142]

Clay materials have the property of carrying cations that can be exchanged for other cations by treatment with a water solution containing the second cation. In the process the structure of the clay material is not changed. This property of base exchange was first observed in soils by H. S. Thompson[143] in 1845 and was studied by J. T. Way[144] about 1850. It may be a property of both the inorganic and organic components of clay materials, but only that of the inorganic portion is considered herein. It is well known that the fertility and tilth of soils and the physical properties of clay materials generally are closely related to the character of the exchangeable base that they contain.

BASE-EXCHANGE CAPACITY

The property of clay materials to carry exchangeable cations is designated as "base-exchange capacity" and is measured in terms of milliequivalents per 100 gm. (1 m.e. $Na_2O = 0.031$ gm.; 10 m.e. per 100 gm. = 0.31 per cent Na_2O). Numerous methods have been suggested for determining base-exchange capacity, but none of them give results of very high accuracy (± 2 m.e. in 70 m.e.). For a detailed discussion of the various methods the works of Hofmann

[141] "The Crystal Structure of the Chlorite Minerals," *Zeitschr. Krist.*, Vol. LXXXVIII (1934), pp. 420–32.

[142] Clay materials also may carry exchangeable anions, but almost nothing specific is known of this property.

[143] "On the Absorbent Power of the Soil," *Jour. Roy. Agric. Soc.*, Vol. XI (1850), p. 68.

[144] "On the Power of Soils To Absorb Manure," *Jour. Roy. Agric. Soc.*, Vol. XI (1850), p. 13.

and Giese,[145] C. du Rietz,[146] Endell and Vageler,[147] and A. N. Puri and H. L. Uppal[148] should be consulted. Of particular significance in the determination of base-exchange capacity is the fact[149] that free aluminum and ferric iron in a clay tend to clog exchange positions and to reduce the base-exchange capacity, and also that extended acid leaching or salt treatment tends to remove aluminum and ferric iron from the lattice to exchange positions,[150] with a resulting reduction in base-exchange capacity.

Methods for the quantitative determination of the specific exchangeable cations yield results of even lower accuracy than the determinations of total exchange capacity, primarily because of the difficulty of separating the easily soluble salts that clay materials may

TABLE 1

BASE-EXCHANGE CAPACITY

(In Milliequivalents per 100 Gm.)

Montmorillonite	60–100	Kaolinite	3–15
Attapulgite	25– 30	Halloysite*	6–10
Illite	20– 40		

* Edelman, in "Relation between the Crystal Structure of Minerals and Their Base-Exchange Capacity," *3d Internat. Cong. Soil Sci.*, Vol. III (1936), pp. 97–99, has published higher values for halloysite; and it must be concluded that the capacity of the mineral is open to some question.

contain. R. P. Graham and J. Sullivan,[151] Hofmann and Giese,[15]. and Endell and Vageler[153] have critically discussed present methods[2]

In Table 1 values for the base-exchange capacity of the common

[145] *Op. cit.*

[146] *The Base-Exchange Properties of Solid Materials* (Stockholm: printed by author, 1938).

[147] *Op. cit.*

[148] "Critical Examination of the Methods of Finding the Base-Exchange Capacity of Soils," *Soil Sci.*, Vol. XLVII (1939), pp. 245–53.

[149] O. C. Magistad, "The Action of Aluminum, Ferrous and Ferric Iron and Manganese in Base Exchange Reactions," *Arizona Agric. Exper. Sta. Tech. Bull. 18* (1928); Endell, Fendius, and Hofmann, "Base-Exchange Characteristics of Clay and Problems of Moldability in Ceramics," *Ber. deutsch. keram. Gesellsch.*, Vol. XV (1934), pp. 595–625.

[150] A. Brammall and J. G. C. Leech, "Base-Exchange and Its Problems," *Sci. Jour. Roy. College Sci.*, Vol. VIII (1938), pp. 43–51.

[151] "Critical Study of Methods of Determining Exchangeable Bases in Clay," *Jour. Amer. Ceramic Soc.*, Vol. XXI (1938), pp. 176–83.

[152] *Op. cit.* [153] *Op. cit.*

clay minerals are given. The spread of values results from the facts that all the members in a single group do not have exactly the same capacity and that for certain clay minerals the capacity varies with particle size.

RELATION TO PARTICLE SIZE

E. A. Hauser and C. E. Reed[154] have pointed out that the base-exchange capacity of montmorillonite does not vary with its particle size, whereas C. G. Harman and F. Fraulini[155] and S. Spiel[156] have shown that the capacity of kaolinite increases with decreasing particle size. These findings are in accord with differences in the structural characteristics of the minerals and the cause of their adsorptive capacity, to be discussed presently. On the same basis it would be expected that the base-exchange capacity of illite would increase with decreasing particle size. W. P. Kelley and H. Jenny[157] report an increase in the exchange capacity of kaolinite, the micas, and montmorillonite by extremely fine grinding. P. Schachtschabel[158] has failed to check this work. Again on the basis of structure, grinding of kaolinite and mica should increase the base-exchange capacity, but an increase for montmorillonite is difficult to understand.

CAUSE OF ADSORPTIVE PROPERTIES OF CLAY MINERALS

Recent work[159] has shown that about 80 per cent of the exchange positions of montmorillonite are on the basal-plane surfaces and that the remainder are on the edges of the flakes. Hendricks[160] has com-

[154] "The Thixotropic Behavior and Structure of Bentonite," *Jour. Phys. Chem.*, Vol. XLI (1937), pp. 911–34.

[155] "Properties of Kaolinite as a Function of Its Particle Size," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 252–58.

[156] "Effect of Adsorbed Electrolytes on Properties of Monodispersed Clay-Water Systems," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 33–38.

[157] "The Relation of Crystal Structure to Base-Exchange in Soils," *Soil Sci.*, Vol. XLI (1936), pp. 367–81.

[158] "Investigation of the Sorption of Clay Minerals and Organic Soil Colloids, and the Determination of the Proportions of These Colloids in Soils by Sorption Methods," *Kolloid-Beihefte*, Vol. LI (1940), pp. 199–276.

[159] Hendricks, Nelson, and Alexander, *op. cit.*

[160] "Base-Exchange of the Clay Mineral Montmorillonite for Organic Cations and Its Dependence upon Adsorption Due to van der Waal's Forces," *Jour. Phys. Chem.*, Vol. XLV (1940), pp. 65–81.

puted that the area per exchange position for one montmorillonite is about 70 A^2. Oxygens with incompletely satisfied valence bonds must exist at the broken edges of flakes, and these have been considered adequate[161] to hold exchangeable cations. Replacement of the hydrogen[162] of hydroxyls exposed at flake edges has also been suggested to account for some of the capacity.

The basal planes of montmorillonite on the Hofmann structure[163] are made up of oxygens that are balanced, and the explanation for holding cations on these planes is not so obvious. It has been suggested that within the lattice[164] substitutions of Mg^{++} for Al^{+++} and of Al^{+++} for Si^{++++} would provide the charge necessary to hold cations. Grim[165] has indicated that substitutions of Al^{+++} for Si^{++++} provide a lattice similar to that of mica which does not expand, probably because the source of the charge is close to the flake surface. Substitution of Mg^{++} for Al^{+++} is considered a more likely explanation because the source of the charge is farther from the surface and, therefore, is adequate to hold a cation but not to prevent the lattice from expanding. A study of analytical data indicates a relation between substitutions in the alumina sheet and base-exchange capacity for some montmorillonite, but for other montmorillonites[166] apparently there is no such relationship. Hofmann and Bilke[167] have suggested that substitution of Al^{+++} for Si^{++++} may be partly balanced by adjustments in the gibbsite sheet, presumably the remainder of the balancing being done by exchangeable cations. On this basis it may be possible to have substitutions in the silica sheet without the development of the mica lattice.

Lattice substitution undoubtedly plays a part in the base-exchange capacity of montmorillonites, but it seems doubtful that it is the entire explanation for the planar exchange capacity, as it

[161] Endell and Vageler, *op. cit.* [162] Kelley and Jenny, *op. cit.*

[163] Hofmann, Endell, and Wilm, *op. cit.*

[164] Hofmann and Bilke, *op. cit.;* Nagelschmidt, "On the Atomic . . . . ," *op. cit.;* Marshall, "Layer Lattices . . . . ," *op. cit.*

[165] "Properties of Clays," *op. cit.*

[166] W. P. Kelley, A. O. Woodford, W. H. Dore, and S. M. Brown, "The Colloid Constituents of California Soils," *Soil Sci.*, Vol. XLVIII (1939), pp. 201–55.

[167] *Op. cit.*

must be if the Hofmann[168] structure is correct. Edelman and Favejee[169] have emphasized this point and consider their structure as explaining more satisfactorily the exchange capacity of montmorillonite. The basal planes of their structure contain (OH) ions which provide hydrogens for replacement by cations.

The generally low base-exchange capacity of kaolinite suggests that the seat of the normal capacity is limited to broken oxygen bonds and/or the hydrogen of hydroxyls at flake edges. Speil[170] has reached a similar conclusion because of the marked change in base-exchange capacity at pH_7. From another point of view, the exchange capacity of kaolinite is low, because there are no replacements within the lattice to set up unbalanced charges and because the mineral does not break down to thin sheets (see later discussion), and hence comparatively few basal plane (OH) ions are exposed for replacement of hydrogen by a cation. Stout's work[171] indicates that certain ions (phosphate) particularly replace the hydrogen of the (OH) ions and effect replacement between the basal planes. For these ions kaolinite has a very high exchange capacity, and when they are present the unit sheets have a random arrangement. Endell and others[172] consider some of the exchange capacity of extremely fine-grained kaolinites to result from lattice distortion.

Similarly, the seat of much of the capacity of illite is at flake edges. However, there are substitutions in the illite lattice which may provide the charge to hold additional cations. Most illite does not break down very readily into extremely small flakes, so that many of the cations held between basal planes because of lattice replacements would not be replaceable. That some of these interplanar cations are replaceable is suggested by the long period of time necessary for illite to reach equilibrium in base-exchange reactions.[173]

CATION REPLACEABILITY

The relative ease of replacement of one cation by another has been the object of much study, and the following series[174] has been

[168] Hofmann, Endell, and Wilm, *op. cit.*

[169] *Op. cit.*

[170] *Op. cit.*

[171] *Op. cit.*

[172] Endell, Hofmann, and Wilm, *op. cit.*

[173] Schachtschabel, *op. cit.*

[174] E. Hauser, *Colloidal Phenomena* (New York: McGraw Hill Book Co., 1939).

widely accepted: $Li^+ > Na^+ \ldots > K^+ > Rb^+ > Cs^+ > Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++} > H^+$. Thus, at equivalent concentrations Ca^{++} will displace a greater fraction of Li^+ than K^+. The divalent ions are more tightly held than the monovalent ones, and J. B. Page[175] has recently provided data to emphasize that ion size is important also in replaceability. According to his data, ions of a size permitting them to fit closely into the cavities inside of the hexagonal net of oxygens are least replaceable; for example, K^+ with a diameter of 2.66 A closely fits the cavity which has a diameter of 2.8 A and is tightly held. Also, it follows from this line of reasoning that the cations are held at the clay-mineral surface rather than at some distance from it, as required by Jenny's[176] concept or by the double-layer idea.[177] According to some advocates of the latter idea, the cations are separated from the clay-mineral particles by an inner layer of (OH) ions. From a structural standpoint this does not seem tenable, since the charges on the lattice are mainly such that positive charges would be required to satisfy them. However, as Kelley and Jenny[178] point out, there are cogent chemical reasons why intermediate (OH) ions should exist if the cation is not exchanged for hydrogen of an (OH) of the lattice itself.

G. Wiegner[179] and many others have attributed the replaceability of cations to differences in the degree of their hydration—the most highly hydrated being held loosest, perhaps, because the hydration hull prevented close contact between the cation and the clay-mineral particle.

Later, in discussing the clay-water system in detail, it will be pointed out that some cations (e.g., Na^+), previously thought to be highly hydrated, probably do not hydrate at all and that other cations hydrate to a lesser degree than has been assumed. Cation exchangeability, therefore, cannot be explained satisfactorily on the basis of cation hydration.

[175] "The Relation of Ionic Size to the Fixation of Potassium and Other Cations by Colloidal Clay" (Ph.D thesis, Ohio State University, 1940).

[176] "Studies on the Mechanism of Ionic Exchange in Colloidal Aluminum Silicates," *Jour. Phys. Chem.*, Vol. XXXVI (1932), pp. 2217–58.

[177] H. Freundlich, *Kapillarchemie* (4th ed.; Leipzig, 1930), Vol. I. [178] *Op. cit.*

[179] "Some Physico-Chemical Properties of Clays," *Jour. Soc. Chem. Ind.*, Vol. L (1931), pp. 65–71, 103–12.

A. L. S. Bar and H. J. C. Tenderloo[180] suggested that cation exchangeability should not be the same for all the clay minerals; and Schachtschabel[181] has recently carefully investigated this point, using known pure clay minerals, and has shown definitely that the relative exchangeability is not the same for all the clay minerals. He shows, for example, that for NH_4-montmorillonite H^+ and K^+ are about equally exchangeable, all the univalent ions, except Rb^+ and Cs^+, are more exchangeable than the divalent ions, and all the divalent ions have about the same exchangeability (Fig. 8). For NH_4-kaolinite (Fig. 9) the exchangeability of the cations is about the same as for NH_4-montmorillonite. NH_4^+, however, is more tightly held by kaolinite. For NH_4-muscovite (Fig. 10) H^+ and K^+ are more tightly held than the divalent ions, and NH_4^+ is even more tightly held than in kaolinite. When a mixture of montmorillonite and muscovite is treated with mixtures of calcium and ammonium acetate, the mica adsorbs relatively much more of the NH_4^+, and the montmorillonite adsorbs relatively more of the Ca^{++}. Hendricks[182] has found that Schachtschabel's results for NH_4^+ and Ca^{++} acceptance by mica and montmorillonite do not hold in all details for all samples of these minerals. He has shown that in mica-montmorillonite mixtures the mica preferentially adsorbs H^+ and the montmorillonite Ce^{+++}.

This recent work shows that the exchangeability series given previously does not hold exactly for the individual clay minerals. Actually there is a series for each clay mineral. Schachtschabel[183] is probably correct in his explanation that the phenomenon results from the difference in the size of the cations in relation to the lattice configurations that give rise to base-exchange (broken bonds, substitutions of Al^{+++} by Mg^{++}, etc.). These findings of Schachtschabel[184] illustrate the great necessity of carrying out clay re-

[180] "On the Double Layer of Clay Colloids," *Kolloid-Beihefte*, Vol. XLVII (1936), pp. 97–124.

[181] *Op. cit.*

[182] Hendricks and Alexander, "Semiquantitative Estimation of Montmorillonite in Clays," *Proc. Soil Sci. Soc. of Amer.*, Vol. V (1940), pp. 95–99.

[183] *Op. cit.* [184] *Ibid.*

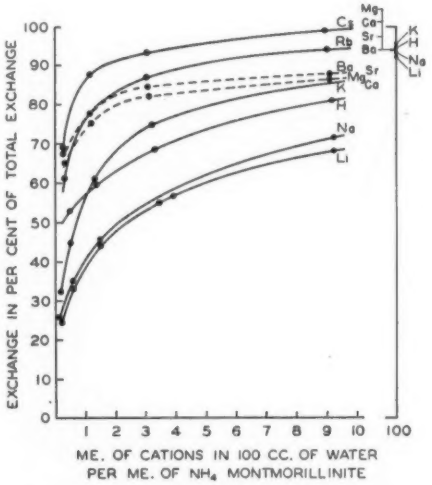

FIG. 8.—NH_4-montmorillonite; ionic exchange with alkali and alkali-earth chlorides. (After Schachtschabel).

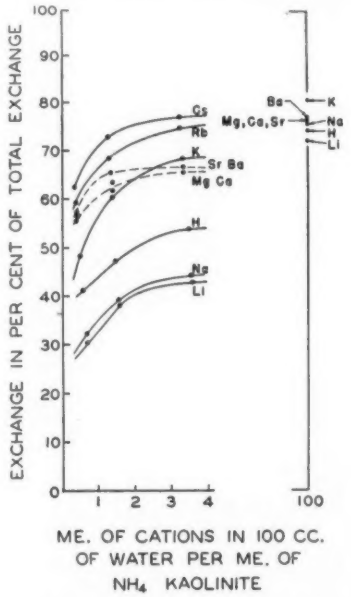

FIG. 9.—NH_4-kaolinite; ionic exchange with alkali and alkali-earth chlorides.(After Schachtschabel.)

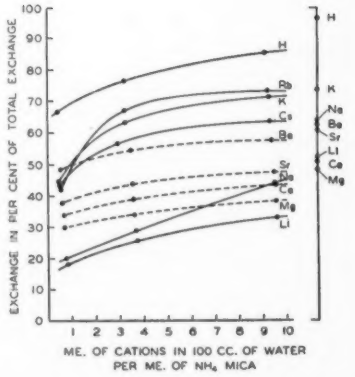

FIG. 10.—NH_4-mica; ionic exchange with alkali and alkali-earth chlorides.(After Schachtschabel.)

searches on material of known clay-mineral composition. Much base-exchange and other chemical work on clays has little value because there is no information on the mineral composition of the material studied.

Recent work by J. E. Gieseking[185] and later by Hendricks[186] has shown that montmorillonite has base-exchange capacity for some large organic cations as well as for inorganic cations. The large organic cations are held between the unit cells in basal planes and practically destroy the swelling of the lattice in the presence of water. The organic cations may be held more firmly than H^+.

CLAY MINERALS—OCCURRENCE

Much data on the composition of various types of argillaceous materials have been published in recent years. No attempt is made to assemble all these data here, but rather to give references to the more important and to deduce from them such general conclusions as appear warranted.

SOILS

Kelley,[187] Hendricks,[188] Bray,[189] and their colleagues in this country, Edelman[190] and his students in Holland and the Dutch East Indies, Hosking[191] and J. Shearer and W. F. Cole[192] in Australasia, C. W. Correns[193] and his students in Germany, and Nagelschmidt

[185] "Mechanism of Cation Exchange in the Montmorillonite-Beidellite-Nontronite Type of Clay Minerals," *Soil Sci.*, Vol. XLVII (1939), pp. 1–14.

[186] "Base Exchange of the . . . . ," *op. cit.*

[187] Kelley *et al.*, "Comparative Study of the Colloid of a Cecil and Susquehanna Profile," *Soil Sci.*, Vol. XLVII (1939), pp. 175–93; "The Colloid Constituents . . . . ," *op. cit.*

[188] Hendricks and Alexander, *op. cit.;* Hendricks and Frey, *op. cit.*

[189] *Op. cit.*

[190] "General Discussions of the Mineralogical Composition of Clays and Qualitative X-ray Analysis of Some Dutch Clays," *Overdruk uit Meded. v. d. Landbouwk.*, Vol. XLIII (1939), pp. 1–39; H. J. Hardon and J. Ch. L. Favejee, "Qualitative X-ray Analysis of the Principal Soil Types of Java," *Overdruk uit Meded. v. d. Landbouwk.*, Vol. XLIII (1939), pp. 1–5.

[191] *Op. cit.*

[192] "X-ray Analysis of Some Tasmanian Soil Colloids," *Jour. Roy. Soc. Western Australia*, Vol. XXVI (1940), pp. 133–37.

[193] "Mineralogical Study of Three Mecklenburg Soils," *Zeitschr. f. Pflanzenern. u. Dungung. u. Bodenk.*, Vol. XLIV (1936), pp. 316–26.

and others[194] in England have led the way in the study of the clay-mineral composition of soils. This work has not yet reached the point of a clear correlation of clay-mineral composition and soil classification based on physical factors or of a precise correlation of environmental factors of soil formation and resulting clay minerals.

Kaolinite, illite, montmorillonite, and halloysite have all been reported in soils, but there is some question regarding the identification of halloysite. It would appear from published data that the halloysite minerals are rare constituents of soils generally. This is not certain, because it is difficult to distinguish between kaolinite and the low hydration form of halloysite.

It is likely that illite is formed infrequently in soils, whereas kaolinite and montmorillonite are commonly formed by soil-forming processes. Illite is present in many soils, but usually as a remnant of the composition of the parent-rock. Kaolinite and montmorillonite may form from the same parent-rock[195] under different environmental conditions. Hosking[196] has shown that in Australia, under conditions of abundant rainfall and active leaching, kaolinite soils form on basic igneous rocks, whereas under conditions of low rainfall and poor leaching montmorillonite soils form from the same igneous rocks.

Some soils contain mixtures of clay minerals, but in many soils there is a single clay mineral that is the dominant component. These are primarily mature soils in which there has been time for the clay mineral to develop, that is, in equilibrium with the environmental factors under which the soil has formed.

Montmorillonitic and kaolinitic soils[197] may form from illitic material, and kaolinitic soils may form from montmorillonite parent-material.[198] As far as the writer is aware, there is no unquestioned example of a montmorillonite soil that has developed from a kaolinite parent-material.

[194] "The Minerals in the Clay Fraction of a Black Cotton Soil and a Red Earth from Hyderabad, Deccan State, India," *Jour. Agric. Sci.*, Vol. XXX (1940).

[195] Nagelschmidt *et al.*, *op. cit.* [196] *Op. cit.*

[197] R. H. Bray, R. E. Grim, W. F. Bradley, and M. M. Leighton, "The Weathering of Loess in Illinois" (unpublished manuscript).

[198] Kelley *et al.*, "Comparative Study of the Colloid . . . . ," *op. cit.*

CONTEMPORANEOUS SEDIMENTS

The work of C. W. Correns,[199] R. Revelle,[200] R. S. Dietz,[201] and Grim and Dietz[202] has made a start in bringing to light the clay-mineral composition of sediments accumulating at the present time on the ocean floors. There appears to be a complete absence of similar data for sediments accumulating today in other environments. Until information regarding these sediments is available, the cycle of changes that argillaceous materials may go through from their source to the site of their accumulation and in later lithification cannot be worked out.

Work to date suggests that illite is the most widely distributed clay mineral in present-day marine argillaceous sediments, that kaolinite is also widely distributed but generally less abundant than illite, and that montmorillonite is usually either absent or of very minor abundance. Dietz[203] suggests that illite is forming in the marine environment of accumulation, perhaps chiefly from montmorillonite. Correns[204] has, however, concluded that there is little transformation of clay minerals on the sea floor.

ANCIENT SEDIMENTS

Sedimentary clays are most frequently mixtures of illite and kaolinite. Occasionally a small amount of montmorillonite is also present, and some of them seem to contain a little halloysite. The Pennsylvanian underclays of Illinois[205] and the Cretaceous and Tertiary clays of the coastal plains are illustrative of the composi-

[199] "Sedimentation in the Deep Sea," *Wissenschaftliche Ergebn. deutsch Atlantischen Expedition auf dem Forschungs u. Vermessungschiff "Meteor,"* Vol. III, Part 3 (Berlin, 1937).

[200] Scripps Inst. of Oceanography, unpublished work. University of California, La Jolla, California.

[201] "Clay Minerals in Recent Marine Sediments" (Ph.D. thesis, University of Illinois, 1941).

[202] "Mineral Composition of Clays from the Floor of the Pacific Ocean off the Coast of California" (unpublished work).

[203] *Op. cit.*

[204] "On the Question of the Formation of Mica in Recent Sediments," *Geol. Rund.*, Vol. XXXIX (1938), pp. 202–22.

[205] Grim and V. T. Allen, "Petrology of the Pennsylvanian Underclays of Illinois," *Bull. Geol. Soc. Amer.*, Vol. XLIX (1938), pp. 1485–1514.

tion of many sedimentary clays. In some clays kaolinite is dominant, in some others illite is most abundant; but usually they are both present in fair abundance. There are some occurrences of sedimentary clays in which other clay minerals are dominant—for example, the Eocene Porter's Creek clay of the Gulf Coast area, containing montmorillonite,[206] and the fuller's earth in the Miocene Hawthorne formation of Georgia and Florida, composed of attapulgite.

In most of the shales that have been studied[207] illite is the dominant clay mineral, and there is some reason to believe that the shaly structure is related to the presence of illite.

The argillaceous material of till and loess, so far as is known, is composed of a mixture of illite, kaolinite, and montmorillonite, with illite the more abundant.

MISCELLANEOUS ARGILLACEOUS MATERIALS

The occurrence of kaolinite minerals in deposits resulting from the action of sulphate waters and of hydrothermal processes has been reviewed by Ross and Kerr.[208] An occurrence of hydrothermal halloysite material has recently been recorded by G. A. Schroter and Ian Campbell.[209] Montmorillonite has also been reported in deposits that are believed to be of hydrothermal origin.[210]

Residual deposits of kaolinite, the precise origin of which has been the subject of much controversy,[211] are widespread and the source of much commercial kaolin. Some of the kaolins are bauxitic in the sense that they contain appreciable amounts of hydrated alumina—for example, boehmite and hydrargillite.

Many bentonite clays formed by the alteration of volcanic ash are

[206] Grim, "Petrography of the Fuller's . . . . ," *op. cit.*

[207] Grim, "Petrographic and Ceramic . . . . ," *op. cit.*

[208] "The Kaolin Minerals," *op. cit.*

[209] "Geologic Features of Some Deposits of Bleaching Clay," *A.I.M.E. Pub. 1139* (1938).

[210] E. Dittler and F. Kirnbauer, "Bentonite at Tomesti, Rumania," *Zeitschr. prakt. Geol.*, Vol. XLI (1933), pp. 121–27; De Lapparent, "Origin of Bentonites from North Africa," *Compt. rend. Soc. geol. de France*, No. 10 (1937), pp. 126–28.

[211] Ross and Kerr, "The Kaolin Minerals," *op. cit.*

composed of montmorillonite clay minerals.[212] Some bentonites also contain cristobalite,[213] and a very small amount of zeolite has also been reported in them.[214]

CLAY MINERALS—REDUCTION OF PARTICLE SIZE ON AGITATION IN WATER

Grim[215] has shown that when clay-mineral particles are agitated in water they tend to break up into smaller-sized units. Because of lattice characteristics, montmorillonite breaks down more readily than kaolinite. Some illites break down easily, whereas others do not. Study of a large number of clays has shown that montmorillonite and some illite minerals readily break down in a suspension into particles less than 0.1 μ in diameter. Kaolinite and most illite minerals are broken down, with difficulty, or not at all, to particles of 1 to 0.1 μ in diameter.

Clearly, in making mechanical analyses of clays the measurements made of particle size represent the degree of disaggregation, and frequently nothing else. Analyses, to be comparable at all, must be made with the same preliminary treatment, including the use of the same electrolyte. Even then, some variation is to be expected if the samples are composed of different clay minerals and have different electrolyte contents.

CLAY MINERALS—OTHER PROPERTIES

The other properties of the clay minerals are not considered here because they are of lesser importance to a consideration of the causes of clay-material properties and the application of such information to practical problems of clay utilization. For those interested in pursuing the subject further the papers of Grim[216] and von Engle-

[212] C. S. Ross and C. W. Shannon, "Minerals of Bentonite and Related Clays and Their Properties," *Jour. Amer. Ceramic Soc.*, Vol. IX (1926), pp. 77–96; A. F. Hagner, "Adsorptive Clays of the Texas Gulf Coast," *Amer. Min.*, Vol. XXIV (1939), pp. 67–107.

[213] J. W. Gruner, "Abundance and Significance of Cristobalite in Bentonites and Fuller's Earths," *Econ. Geol.*, Vol. XXXV (1940), pp. 867–75.

[214] M. N. Bramlette and E. Posnjak, "Zeolitic Alteration of Pyroclastics," *Amer. Min.*, Vol. XVIII (1933), pp. 167–71.

[215] "Properties of Clays," *op. cit.*

[216] "Properties of Clays," *op. cit.*

hardt[217] should be consulted for optical properties; the work of Kelley and others,[218] for dehydration characteristics; the work of J. Orcel[219] and F. H. Norton,[220] for thermal analyses; the work of Grim and Bradley[221] and L. Tscheischwili and others,[222] for the changes in the clay minerals when they are fired; and the summary of W. Noll,[223] for the physical chemical conditions under which the clay minerals may be formed.

CLAY-WATER SYSTEM

The most important properties of clays are plasticity, green bonding strength, drying shrinkage, compaction, thixotropy, and viscosity of clay and water suspensions—that is, properties of clay material in the presence of water. It is obvious that a satisfactory understanding of these properties awaits precise concepts of the clay-water system. It is the object of the remainder of this report to analyze the available pertinent data and to draw from them such general concepts of clay-water structure and relationships as seem warranted. The analysis will be limited to clay-water mixtures in the plastic state.

F. Grout[224] early indicated that the most satisfactory explanation of the plastic properties of clays was based on the concept of a film of water enclosing the particles making up the clay. Many workers[225] have emphasized the importance of flake-shaped constituent

[217] *Op. cit.*

[218] "Hydration of Minerals and Soil Colloids in Relation to Crystal Structure," *Soil Sci.*, Vol. XLI (1936), pp. 259–74.

[219] "Differential Thermal Analyses in the Determination of the Constituents of Clays, Laterites, and Bauxites," *Cong. Internat. Mines, Met., geol. Appl.* 7 (1935), pp. 359–71.

[220] "Critical Study of the Differential Thermal Method for the Identification of Clay Minerals," *Jour. Amer. Ceramic Soc.*, Vol. XXII (1939), pp. 54–63.

[221] "Investigation of the Effect of Heat on the Clay Minerals Illite and Montmorillonite," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 242–48.

[222] "Metakaolin," *Ber. deutsch. keram. Gesellsch.*, Vol. XX (1939), pp. 249–76.

[223] "Mineral Formation in the System $Al_2O_3 \cdot SiO_2 \cdot H_2O$," *Neues Jahrb. f. Min.*, Vol. LXX, Abt. A (1935), pp. 65–115; "On the Conditions under which Kaolinite, Montmorillonite, Sericite, Pyrophyllite, and Analcim Can Form," *Min. u. Pet. Mitt.*, Vol. XLVIII (1936), pp. 210–46.

[224] "The Plasticity of Clay," *Trans. Amer. Ceramic Soc.*, Vol. XIV (1912), p. 71.

[225] C. Terzaghi, "The Physical Properties of Clay," *Tech. Engineer. News*, Vol. IX (1928), pp. 10, 11, 36.

particles of clays in explaining their plastic properties; and later work, particularly on the clay minerals, has substantiated both the existence of flake-shaped particles in clay materials and their importance in explaining the physical properties of these materials.

At the present time there are few students of clays who would dispute the premises that clays are composed of flake-shaped particles, that these flake-shaped particles are encased in water envelopes when the clay is in the plastic state, and that the plastic properties of clays depend to a very large degree on the characteristics of the water envelopes. By "characteristics" are meant such things as thickness, density, and orientation of the water molecules. Plasticity may be considered as a consequence of a binding force between particles tending to hold the whole mass together and a water film that separates the flakes, thereby weakening the binding force and acting as a lubricant between them. Plastic deformation is the sum total of the movement of flakes with respect to each other, the actual movement taking place in the water film.

STATE OF THE WATER IN THE ENVELOPE

Based on the work of I. Langmuir,[226] who investigated the orientation and packing of polar molecules in adsorptive films, Terzaghi[227] and others have conceived of the water envelope as being built up of layers of uniformly oriented water dipolar molecules. Slippage within the water film was postulated as occurring in the planes of the dipole ends. The idea has been held that the water of the envelope immediately adjacent to the clay-particle surface had a higher density than ordinary water, and some data in support of such increased density have been presented. On the basis of the oriented dipole concept and the increased density at the surface it was postulated that the innermost layers of dipoles were very closely packed and that the closeness of packing decreased outward.[228] R. Houwink[229] has, however, concluded that there is no increased viscosity; and W. Nitzsch[230] has presented experimental evidence

[226] "The Constitution and Fundamental Properties of Solids and Liquids," *Jour. Amer. Chem. Soc.*, Vol. XXXIX (1917), pp. 1848–1906.

[227] *Op. cit.* [228] Grim, "Relation of Composition . . . . ," *op. cit.*

[229] *Elasticity, Plasticity, and Structure of Matter* (Cambridge: University Press, 1937).

[230] "On the Structure of the Hydration Hull of Inorganic Soil Colloids," *Kolloid Zeitschr.*, Vol. XCIII (1940), pp. 110–15.

that the first water added to dried clay materials assumes a density less than 1 and that, as more water is added, the density gradually rises to 1. According to the latter author, the swelling water of montmorillonite has a density less than 1. Recent ideas of the structure of the water film are more in accord with the findings of Houwink and Nitzsch.

Investigations of the hydrogen bond have led recently to a better understanding of the structure of the water molecule.[231] On the basis of this work Hendricks and Jefferson[232] have presented a con-

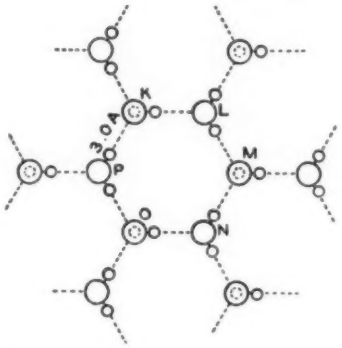

FIG. 11.—Hexagonal net of water molecules. Large spheres represent oxygen atoms and small spheres hydrogen atoms; dotted lines indicate bonding through hydrogen. (After Hendricks and Jefferson.)

cept of the structure of the water in the films. In the language of Hendricks and Jefferson a water layer is composed of water molecules joined into hexagonal groups of an extended hexagonal net as shown in projection in Figure 11. The arrangement is partly a result of a tetrahedral distribution of charge about a water molecule, two corners of the tetrahedron being occupied by hydrogen atoms and the other two corners by an excess of electrons. Each side of the hexagon (Fig. 11) must correspond to a hydroxyl bond, the hydrogen-oxygen bond of one water molecule being directed toward the

[231] J. D. Bernal and H. D. Megaw, "The Function of Hydrogen in Intermolecular Forces," *Proc. Roy. Soc. London*, Ser. A., Vol. CLI (1935), pp. 384–420. J. M. Burgers, "Introductory Remarks on Recent Investigations concerning the Structure of Liquids," *Second Rept. on Viscosity and Plasticity* (Amsterdam, 1938).

[232] *Op. cit.*

negative charge of a neighboring molecule. One-fourth of the hydrogen atoms, or a hydrogen atom of half the water molecules, are not involved in bonding within the net (*K*, *M*, and *O* of Fig. 11). Hendricks and Jefferson[233] visualize the net as being tied to the silicate sheet of the clay mineral by the attraction of those hydrogen atoms not involved in binding within the net and the oxygen atom of the neighboring silicate sheet (Fig. 12). When the surface of the clay mineral contains hydroxyl groups (e.g., kaolinite), part of the hydroxyls are free for binding through hydrogen to oxygen atoms in the water layer.

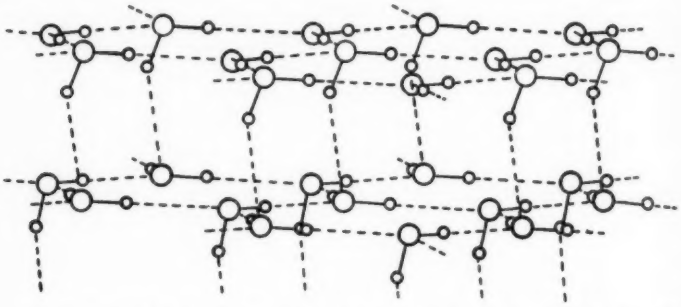

FIG. 12.—Probable structure of multiple water layers. (After Hendricks and Jefferson.)

The net has just the *a* and *b* dimensions of the silicate layer minerals if the separation of the oxygen atoms of the water molecules is about 3.0 A in projection. It is assumed that the oxygen atoms are in one plane. In this configuration there are four molecules of water for each layer in the unit structure instead of six, as in the close-packing arrangement of the older concept.[234]

The stability of the layer arises from its geometrical relationship to oxygen ions of the silicate framework (Fig. 12). Presence of the first layer favors the formation of a second, and the structure is then propagated away from the surface. The dissociation pressure of successive layers considered as hydrates would finally approach the vapor pressure of water at the temperature of observation.

[233] *Op. cit.*

[234] Bradley, Grim, and Clark, *op. cit.;* Nagelschmidt, "On the Lattice . . . . ," *op. cit.*

Kelley and his colleagues[235] have developed the concept that there are two types of adsorbed water in clays. One type, designated as "planar water," coats the plane surfaces of the flakes, is loosely held, and, as a consequence, is lost at low temperatures (−150° C.). The other type, known as "broken-bond water," is more tightly held at the edges of the sheets. Strong evidence has been presented for this concept, and it seems to fit into explanations of the plastic properties of clays.

Planar water could well have the configuration described by Hendricks and Jefferson,[236] whereas broken-bond water would be expected to have such a regular molecular orientation to a much less degree. In montmorillonite, planar water would be the dominant type; but in kaolinite and illite, broken-bond water, although not necessarily dominant, would play a more important role than in montmorillonite.

FACTORS DETERMINING THE STATE OF WATER IN THE ENVELOPE

Many investigators, but particularly Wiegner[237] and Endell, his colleague,[238] have considered that the adsorbed cations are hydrated and that a union of the solvation hulls forms the water envelope around clay-mineral particles. According to this idea, the thickness and other characteristics of the water film are a direct consequence of the hydration of the adsorbed cations that are present. This idea has become so prevalent that it has been widely accepted without critical study of the evidence for and against it.

In Table 2 values are given for the size of hydrated cations and the hydration in molecules of water per ion that have been suggested by several workers. It is obvious that there is considerable divergence in the values given by different workers and even differences in the order of hydration of the cations.[239] Attempts to measure the degree of hydration of the cations, therefore, have not provided strong evidence that the cations are actually hydrated.

J. D. Bernal and R. H. Fowler[240] some years ago presented data

[235] "Hydration of Minerals . . . . ," *op. cit.*

[236] *Op. cit.*

[237] *Op. cit.*

[238] Endell and Vageler, *op. cit.*

[239] Bar and Tenderloo, *op. cit.*

[240] "A Theory of Water in Ionic Solution with Particular Reference to Hydrogen and Hydroxyl Ions," *Jour. Chem. Phys.*, Vol. I (1933), pp. 515–48.

that threw doubt on the hydration of some cations. Bar and Tenderloo[241] have enumerated difficulties encountered by explanations of clay properties based on cation hydration, and L. D. Baver[242] has summarized experimental data on the swelling and heat of wetting of soil colloids that do not fit well with cation hydration. Hendricks and others[243] have recently presented strong evidence that

TABLE 2

ION SIZES AND IONIC HYDRATION*

	IONIC RADII IN ANGSTROMS				HYDRATION (MOLE H_2O)				
	Not Hydrated		Hydrated						
	A	B	C	D	E	F	G	H	I
Li	0.68	0.78	10.03	7.3	12.6	10	15	11–13	13–14
Na	0.98	0.98	7.90	5.6	8.4	5	8	9–11	8–9
K	1.33	1.33	5.32	3.8	4.0	1	4	5–6	5
NH_4	.....	1.43	5.37	.....	4.4	.....	.....	2–3	.....
Rb	.....	1.49	5.09	3.6	.....	0.5	.....	.....	.....
Cs	.....	1.65	5.05	3.6	.....	0.2	.....	.....	.....
Mg	0.89	0.78	.....	10.8	13.3	33	21	20–23	.....
Ca	1.17	1.06	.....	9.6	10.0	22	22	19–22	.....
Sr	1.34	1.27	.....	9.6	8.2	21	.....	.....	.....
Ba	1.49	1.43	.....	8.8	4.1	17	14	18–20	.....
Al	0.79	0.57	.....	.....	.....	.....	57	.....	.....
La	1.30	1.22	.....	.....	.....	.....	30.5	.....	.....

* As suggested by the following authors:

A.— W. H. Zachariassen, *Zeitschr. Krist.*, Vol. LXXX (1931), p. 137.
B.— V. Goldschmidt, *Vid. Nordsk. Akad. Oslo, Skr. math.-naturv. kl.*, Vols. VII, VIII (1926, 1927).
C.— H. Jenny, *Jour. Phys. Chem.*, Vol. XXXVI (1935), pp. 2217–58.
D, F.— H. Pallman, *Bodenk Forsch.*, Vol. VI (1938), p. 21.
E.— H. Remy, *Zeitschr. Phys. Chem. Abt.*, A, Vol. XXXIX (1915), p. 467.
G.— H. Brintziner and C. Ratanarat, *Zeitschr. anorg. allgem. chem.*, Vol. CCXXII (1935), p. 119.
H.— F. Bourion, E. Ronyer, and O. Hun, *Compt rend. Acad. sci.*, Vol. CCIV (1937), p. 1420.
I.— J. Baborovski, J. Velisch, and A. Wagner, *Jour. chim. phys.*, Vol. XXV (1928), pp. 452–82.

certain of the cations (Na^+) that were thought to be highly hydrated are probably not hydrated at all. In addition, Houwink[244] has stated that the thickness of the water film (10^2–10^3 A) is too great to be accounted for by the hydration of adsorbed cations, and Speil[245] has concluded that solvation of the adsorbed cations cannot explain fully the presence of water films. It seems, therefore, that the gen-

[241] *Op. cit.*

[242] *Soil Physics* (New York: John Wiley & Sons, 1940).

[243] *Op. cit.* [244] *Op. cit.* [245] *Op. cit.*

eral conclusion is not justified that all the common adsorbed cations are hydrated, and that some other cause for the development of the water film around the clay particles must be sought.

The lattice structures of the clay-mineral particles are continuous in the *a* and *b* crystallographic directions, so that the edges of the flakes would contain broken bonds or unsatisfied valence charges that would serve to hold water perhaps through a hydrogen bond. The explanation of the planar water is not so simple. For example, in montmorillonite, according to the structure of Hofmann and others, the basal planes are oxygens without any unsatisfied charges, and there is no obvious good reason why thick films of water should develop on them. Substitutions may occur within the lattice that develop charges on the surface, but it is believed that they are satisfied with adsorbed cations. Kelley and others[246] have suggested that planar water is due to the existence of stray forces without accounting for their source. It does not seem likely that stray forces are entirely adequate to account for the thicknesses of water films that are known to form.

According to the structure of the water sheet worked out by Hendricks and Jefferson,[247] the water is held to the clay minerals through hydroxyl bonds to oxygens or hydroxyls, and it propagates itself because of its configuration. This provides a reason for the development of a water film, but it does not explain the difference in the development of the water layers in different minerals. For example, it does not explain why montmorillonite develops such thick water sheets and pyrophyllite does not.

If one assumes that the correct structures of montmorillonite and halloysite are those suggested by Edelman and Favejee,[248] that the concept of the structure of the water layers of Hendricks and Jefferson[249] is correct, and that the oriented layers can only develop when the surface of the flakes carry projecting (OH) ions, a general concept of clay-mineral-water can be worked out that seems eminently satisfactory.

[246] "Hydration of Minerals . . . . ," *op. cit.*

[247] *Op. cit.*

[248] "On the Crystal Structure . . . . ," *op. cit.*

[249] *Op. cit.*

According to this idea, the oriented sheets of water are tied to the projecting (OH) ions of the basal sheets in montmorillonite. Montmorillonite swells because the units of the clay mineral are pushed apart by the growth of additional sheets of water (unless *certain* adsorbed cations are present that bind the sheets together, as will be discussed presently). Similarly, a water sheet develops between the layers of halloysite. In this mineral a plane of (OH) ions is adjacent to the projecting (OH) ions in the next structure unit, and this may explain why the sheet is restricted to a single layer. It must be confessed, however, that this explanation of the extra water in halloysite is no more satisfactory than those based on other concepts. Further study is necessary before the structural attributes of the halloysite minerals become well known.

Kaolinite does not develop a sheet of water between the unit cells because it does not have projecting (OH) ions.

In the case of illite, as in that of kaolinite, there are no projecting (OH) ions, and the mineral does not develop planar water between the unit cells. In natural clay materials flake-shaped particles of illite and kaolinite exist that are many unit cells thick. On the flat surfaces of these particles a water film develops. According to the suggested concept, this water would be expected to differ from water held on the flat surfaces of montmorillonite particles. For illite and kaolinite the water molecules would be oriented little or not at all, and, as a consequence, the water sheet would not develop to any considerable thickness. Stray forces that are a consequence, perhaps, of slight distortions or irregularities of the lattice may serve to hold such water.

It follows from this concept that the water envelope of a single clay mineral consists of parts held by forces of varying intensity in which the water molecules are arranged differently, and also that the amount of water molecule orientation and the binding forces vary for the different clay minerals. Thus, for kaolinite and illite there is relatively more broken-bond water than for montmorillonite. In addition, the planar water for montmorillonite differs from that of kaolinite and illite because it is made up of oriented water molecules, because it is more tightly held, and because it may extend greater distances from the flake surfaces.

INFLUENCE OF ADSORBED CATIONS ON THE WATER FILM

It has been pointed out that it is highly questionable whether some of the cations previously thought to be highly hydrated actually are hydrated at all. It is equally questionable whether other cations hydrate to the degree that has been postulated. There remain to be analyzed other ways in which adsorbed cations may affect the water film.

Jenny[250] and, later, J. D. Sullivan[251] have pointed out that ions of large volume would occupy more space than ions of lesser volume and, consequently, that when large ions are present there would be less space available for water molecules. Thus, 1 Ca^{++} of volume 4.99 A^3 will replace 2 Na^+ with a combined volume of 7.88 A^3. However, in view of the facts that the cations are smaller than the water molecules and that the water molecules are packed loosely, it appears unlikely that a clogging effect is important.

It has long been believed that adsorbed cations exert a polarizing effect on the water of the film. According to Jenny,[252] the polarizing effect is stronger the greater the charge and the smaller the radius. Burgers[253] has suggested that adsorbed cations exert a tightening effect on the configuration of the water sheet. Perhaps this is not at variance with the polarizing effect, although it must be admitted that the precise effect of cations on the configuration of the water molecules is not clear.

Data from investigations of the relation of exchangeable bases to plastic properties indicate that in some way the character of the adsorbed cation affects the thickness of the water film. In the absence of hydration of the cations it seems likely that the effect is produced by a binding action of the cations. That is to say that cations act as bridges to bind the clay-mineral sheets together. The action is analogous to the effect of K^+ in holding together the unit cells of muscovite in the direction of the *c*-axis. This idea does not preclude a slight hydration of certain ions, but it postulates the

[250] "Cation and Anion Exchanges on the Interface of Permutite," *Kolloidchem.*, Vol. XXIII (1927), pp. 428–72.

[251] "Physico-chemical Control of Properties of Clay," *Trans. Electrochem. Soc.*, Vol. LXXV (1939), pp. 71–97.

[252] "Studies on the Mechanism . . . . " *op. cit.* [253] *Op. cit.*

adsorbed cations as controlling the thickness of the film water primarily by means of the force with which they hold the sheets together.

In applying this idea to montmorillonite it follows that the thickness of the water film is the result of two opposing forces: (*a*) the tendency of layers of water to develop on the basal planes, for reasons already discussed; and (*b*) the tendency of the adsorbed cations to hold the sheets together. The resulting thickness of the film is chiefly dependent on the cation. The bonding action of the adsorbed cations is not a new concept, but its significance has perhaps not been appreciated fully.

It may be postulated that the bridging action of the adsorbed cations varies with their valence and perhaps also with their size. With regard to the latter factor, the work of Page[254] suggests that, for ions of equal valence, those with a diameter about equal to that of the hole in the hexagonal net of the silica sheet would exert the greatest bonding action.

It is a well-known fact that Na-montmorillonite expands greatly in the presence of abundant water, whereas under similar conditions Ca-montmorillonite expands very little. According to this concept, the great swelling of the Na-montmorillonite is due not to the hydration of the Na^+ serving as a wedge to force the layers apart but to the absence of a strong bridge because of the univalent character of Na^+ and perhaps also because of its small size enabling it to fit well in the hole of the silica sheet. The Ca-montmorillonite does not expand greatly because of the slight hydration of Ca^{++} but because the divalent ion holds the layers together so that a thick series of water sheets cannot form between them.

It is also a well-known fact that completely electrodialyzed montmorillonite expands only very slightly. On the basis of the above concept, it would seem at first that the H-montmorillonite should swell more avidly than Na-montmorillonite. That, perhaps, would be true if H-montmorillonite contained only H^+ as the adsorbed cation. There is a considerable body of data to indicate that, before all the adsorbed cations are replaced by H^+, some Al^{+++} is removed

[254] *Op. cit.*

from the lattice to occupy exchange positions. Many workers[255] have presented experimental evidence for this point. An explanation for the nonswelling of so-called "H-montmorillonite clays" is that they are not pure H-montmorillonites but also contain multivalent cations that serve to bind the layers together.

What has been said has been developed with particular reference to montmorillonite clay materials. It can also be applied to clay materials composed of other clay minerals. In illites and kaolinites the water does not penetrate between the basal planes of the unit cells. The planar water occurs on aggregates and, as pointed out before, is probably held by weaker forces than those operating in montmorillonite. Likewise, illite and kaolinite have low capacity for holding adsorbed cations, so that the forces holding the clay-mineral aggregates to each other would be less than in montmorillonite clay materials. It may be concluded that the total area encased by water in illite and kaolinite clay materials would be less than in those composed of montmorillonite. It can also be concluded that a smaller part of the total water of illite and kaolinite clay materials would show a definite configuration than of montmorillonite clay materials and that the configuration would be less regular in the former types of materials than in the latter types.

PLASTIC PROPERTIES OF CLAY MATERIALS ON THE BASIS OF THE FOREGOING CONCEPT

Clays composed of illite and kaolinite clay minerals tend to adsorb less water, to have lower green bonding strength, as expressed in terms of modulus of rupture of the clay alone or when determined for sand-clay mixtures, to be more permeable to water, and to shrink less and more rapidly than clays composed of montmorillonite.[256] These differences in properties would be expected on the basis of the concept outlined.

Sullivan and Graham,[257] G. J. Barker and E. Truog,[258] and Speil[259]

[255] Hendricks and Alexander, *op. cit.;* Hofmann and Giese, *op. cit.;* G. Volk, "Nature of Potash Fixation in Soils," *Soil Sci.*, Vol. XLV (1938), pp. 263–76.

[256] Grim, "Relation of Composition . . . . ," *op. cit.*

[257] *Op. cit.*

[258] "Improvement of Stiff Mud Clays through pH Control," *Jour. Amer. Ceramic Soc.*, Vol. XXI (1938), pp. 324–29.

[259] *Op. cit.*

have shown that clays carrying Na^+ require less tempering water than H^+ clays to attain the same degree of stiffness or the same yield-point when force is applied to the plastic mass. Stated another way, if clays of the same water content are compared, the Na-clay will be less stiff and will yield with lower applied pressure than the H-clay. The order of increasing yield-point (ability to hold shape) with a given water content is approximately as follows:[260] Li^+, Na^+, Ca^{++}, Ba^{++}, Mg^{++}, Al^{+++}, K^+, Fe^{+++}, NH_4^+, H^+. In this series there is considerable difference between the effect of Li^+ and Na^+ and that of Ca^{++}. The difference between the other members of the series is not very great. This series is in agreement with expected results if it is considered that the so-called "H-clays" carry Al^{+++}. The position of Li^+ and Na^+ would be a consequence of their low power to bind the clay-mineral flakes together. Little water would therefore be required between the sheets for the mass to yield; or, if much water were present, the mass would yield with low applied pressure.

Na-clays are reported[261] to show very high Atterberg Plastic Indices that result from very low Lower Plastic Limits and very high Lower Liquid Limits. From what has just been said, the value for the Lower Plastic Limit would be expected. Also, the high value for Lower Liquid Limit would be expected in the absence of multivalent cations binding the clay mineral particles together and impeding the full development of the water envelope.

Extensive data regarding the effect of exchangeable cations on bonding strength are not yet at hand. Available data suggest that the strength in the green (i.e., moist) condition is greater for Ca- and H-clays than for Na-clays and that the reverse relationship is true for strength in the dried[262] but unfired condition. The green-strength relationship is clear on the basis of the low bonding power of Na^+, but the explanation for the dry-strength relationship is not

[260] J. D. Sullivan and R. P. Graham, "Effect of Exchangeable Bases on Torsion Properties of Clay," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 39–51.

[261] Endell, Fendius, and Hofmann, *op. cit.*

[262] Speil, *op. cit.;* Graham and Sullivan, "Effect of Base-Exchange on Absorption and Transverse Strength of Clay Bodies," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 52–56.

entirely clear, unless it is considered that dry strength is a function of the total available surface area of the clay-mineral particles. With the low bonding power of the particles for each other in the Na-clay the tendency would be for the component clay-mineral particles to disaggregate and form a huge surface area per volume of clay.

It is well known[263] that Na-clays dry more slowly than Ca- or H-clays. An explanation is that the water in the Na-clay penetrates more completely between sheets; or, stated another way, the clay-mineral units separated by the water are smaller and the water itself occurs in smaller spaces. A further factor that may be of importance is that in Na-clays there is little binding force between the clay-mineral flakes to speed up drying by squeezing action on the water.

Speil[264] has shown that substitution of Na^+ for H^+ on a kaolinite clay tends to decrease both the pore water and shrinkage water. The suggested explanation, in addition to that already given, is that particles with low attractive forces between them (Na-clay) could come into a more compact arrangement, whereas particles with high attractive forces between them would be pulled together into a random arrangement before they reached the most compact positions. The random arrangement would be expected to give a relatively higher pore-water value.

Na-montmorillonite adsorbs water and is much less permeable than Ca-montmorillonite. The high water adsorption of Na-montmorillonite is expected because the flakes are held together loosely, so that a large amount of water can enter between them. The low permeability is in accordance with the discussion of rate of drying.

It would seem, therefore, that the suggested concept agrees with certain important plastic properties of clays. Whether it is successful in explaining all or even most of the plastic properties of clays remains to be determined by future work.

[263] Sullivan and Graham, "Effect of Exchangeable Bases on the Drying of Clay Bodies," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 57–61; C. G. Harman, "Physical and Chemical Characteristics of Clay Related to Their Working Properties," *Brick and Clay Rec.*, Vol. XCIV (1939), pp. 26–27.

[264] *Op. cit.*

LATTICE STRUCTURE OF CLAY MINERALS AND SOME PROPERTIES OF CLAYS[1]

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ABSTRACT

Minerals appearing in clays generally have layer lattice structures formed from (1) uncharged layers with hydroxyl ions on both surfaces, (2) hydroxyl ions on one surface and oxygen ions on the other, (3) oxygen ions on both surfaces; (4) charged layers with oxygen ions on both surfaces; or (5) two types of layers, one with hydroxyl ions on both surfaces and the other with oxygen ions on both surfaces. The discussion is limited to (class 2) kaolin minerals, serpentines, and cronstedtite; (class 3) pyrophyllite, and talc; (class 4) hydrous micas (illite, bravaisite, pholidolite, glauconite, celadonite) and the montmorillonite-nontronite group of minerals. Some new information on the montmorillonite-nontronite group, anauxite, and chrysotile is summarized.

Factors limiting composition, base exchange, polymorphism, crystal size, and behavior toward water are discussed.

INTRODUCTION

It was my pleasure to study Dr. Grim's paper on "Modern Concepts of Clay Materials" before preparation of this address. He has very thoroughly reviewed most of the published information on clay minerals and has discussed their lattice structures in some detail. This covered the well-explored territory leading to a frontier of knowledge in geological and pedological sciences, and I have no alternative but to cross that frontier. One must not forget that in exploration of new territories the best passes might not first be selected and the traveler, because of error, might leave his bones whitening by the way or washed by the floods that were too swift for him to cross.

SUPERPOSITION OF SILICATE LAYERS

Structural features of the silicate layer minerals present three major problems: (1) What are the atomic arrangements in the individual layers? (2) How are the layers superimposed in a particular mineral? (3) How are the compositions of individual minerals influenced by isomorphous replacements, and what factors determine base exchange?

[1] Address delivered at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941.

Let me start with a part of the third of these problems—the question of isomorphous replacements. This has been answered in a qualitative way by early mineralogical work, which was given a rational explanation by the contributions of C. Maugin[2] on the composition of micas and the more extensive work of W. L. Bragg[3] on silicate minerals. Quantitative estimates of variation limits for compositions of clays and other layer silicate minerals, however, have not yet been published. Work of this character for the montmorillonite group of minerals will be discussed.

Dr. Grim has described the atomic arrangements within the layers of the various minerals, the essential description of which started with the fundamental work of L. Pauling.[4] Here we shall discuss only the manner in which layers are superimposed in the several lattices, for these influence the properties of clays to a great extent. Considerable polymorphism was found by C. S. Ross and P. F. Kerr[5] for the kaolin minerals—kaolinite, dickite, nacrite, and halloysite; and recent work has shown that the octophyllite micas occur in at least six forms.[6] A most significant advance has been the discovery of indefinite sequences in layer successions where several arrangements can be realized, in which the relative positions of atoms that are closest neighbors in adjacent layers remain unchanged. This effect, which has been demonstrated for the micas, kaolins, pyrophyllite, and talc, is probably most simply illustrated by graphite, in which, however, it has not yet been sought.

The atomic arrangement parallel to the perfect cleavage in a carbon layer of graphite is shown in Figure 1. A second layer of carbon atoms above the first can be in either the position *A* or the position *B*—the two positions being indistinguishable when only two layers are present. In layers beyond the second, however, there can be a random choice between arrangement *A* and *B* instead of the exact

[2] "Studies on Muscovite Mica by Means of X-Rays," *Compt. rend.*, Vol. CLXXXV (1927), p. 288; Vol. CLXXXVI (1928), p. 186.

[3] *Atomic Structure of Minerals* (Ithaca, N.Y.: Cornell University Press, 1937).

[4] "The Structure of Micas and Related Minerals," *Proc. Nat. Acad. Sci.*, Vol. XVI (1930), pp. 123–29.

[5] "The Kaolin Minerals," *U.S. Geol. Surv. Prof. Paper 165-E* (1931), p. 172.

[6] "Polymorphism of the Micas," *Amer. Min.*, Vol. XXIV (1939), pp. 729–71.

succession required for an ordered crystal. Occurrence of this random arrangement would give rise to diffuse diffraction phenomena of the type observed for micas, pyrophyllite, talc, chlorites, stilpnomelanes, and other minerals.

If more than one kind of layer is present as in vermiculite, the hydrated form of halloysite, and anauxite, there can possibly be an indefinite sequence of kinds of layers. This has been demonstrated by J. W. Gruner[7] for mica-vermiculite crystals, in which interlayer positions are randomly those of mica or vermiculite in a succession

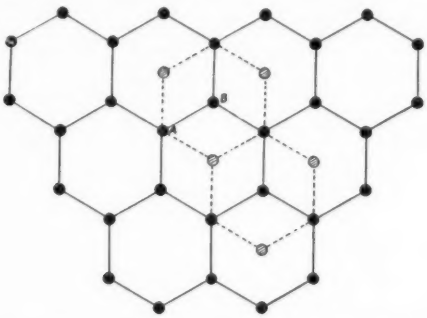


FIG. 1.—Atomic arrangement in a carbon layer of graphite. Atoms in adjacent layers (*shaded*) can be above either *A* or *B*, but only above one of them in an ordered crystals. Irregular layer successions involving both *A* and *B* would give disordered lattices similar to those of some layer silicate minerals.

of layers. An analogous situation is found for the alloys of graphite with the alkali metals.[8]

It is perhaps apparent that the forces between layers, which are important in determining the useful physical properties of clay minerals, are strongly dependent on the possible charge of the layer and on the character of its surface atoms. The greatest attraction per unit surface is between charged surfaces as found in the micas and chlorites and the least between uncharged surfaces containing oxygen atoms. Layers having hydroxyl ions on at least one surface—the

[7] "The Structures of Vermiculites and Their Collapse by Dehydration," *Amer. Min.*, Vol. XIX (1934), pp. 557–75.

[8] U. Hofmann, "Graphite and Graphite Compounds," *Ergebn. d. exakt. Naturwiss.*, Vol. XVIII (1939).

kaolin minerals, for instance—occupy intermediate positions due to the considerable strength of the hydrogen bond. In the kaolin minerals each hydroxyl group in the bottom of a silicate layer approaches most closely to a single oxygen atom of a silicate group in the top of an adjacent layer, ostensibly forming a hydrogen bond. If oxygen atoms are in both surfaces, they pack as tightly together as possible, each oxygen atom having two nearest neighbors in the adjacent surface. This is the situation for both talc and pyrophyllite.

KAOLIN-TYPE MINERALS

Among the minerals having the composition $Al_2Si_2O_5(OH)_4$, listed in Table 1, only nacrite has a completely ordered sequence of layers. It is probably the stable modification that can seldom be realized, and it has been found in only two localities, on account of the greater entropy of the unordered arrangements. There is no reason at the present time for considering halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) to have types of layers different from kaolinite, nacrite, and dickite. New evidence, however, might be found that would lead to a more complete understanding of its structure. The powder-diffraction pattern of halloysite differs somewhat from that of kaolinite, but in a manner that can be accounted for by its degree of organization. This factor has particularly great influence on intensities of reflections from planes with the l index other than zero.

Cronstedtite, chrysotile, and antigorite are of particular interest in that they bear the same formal relationship to the usual kaolin minerals as do the octophyllite to the hetaphyllite micas. In other words, the positions having octahedral co-ordination are completely filled. Cronstedtite, further, has an unusual composition, in which silicon in tetrahedral co-ordination with respect to oxygen is apparently isomorphously replaced by ferric iron. This is only apparent, however, for the cation to oxygen distance is appreciably increased when iron is present and half of the possible positions must be filled. The increased lattice dimensions arising from the presence of iron in the tetrahedral co-ordination positions, as well as the decrease in positive charges, make possible complete filling of the octahedral positions. Such a mineral could form only in an environment having a high amount of iron in solution with a very restricted

value of its oxidation-reduction potential. It would never be expected in the usual clays.

A structure for chrysotile asbestos was advanced by Bragg and B. E. Warren,[9] which satisfactorily explained its fibrous character. However, many of us, including Warren, knew that some of the X-ray diffraction data were not satisfactorily explained by this struc-

TABLE 1

LAYER MINERALS WITH OXYGEN IONS IN ONE SURFACE AND HYDROXYL IONS IN THE OTHER

MINERAL	COMPOSITION AND CO-ORDINATION			LACK OF ORDER IN THE STACKING OF LAYERS
	Octahedral	Tetrahedral		
	Single Kind of Layer—Uncharged			
Nacrite	$(Al)_2$	$(Si)_2$	$O_5(OH)_4$	None
Dickite	$(Al)_2$	$(Si)_2$	$O_5(OH)_4$	Slight
Kaolinite	$(Al)_2$	$(Si)_2$	$O_5(OH)_4$	Considerable
Halloysite	$(Al)_2$	$(Si)_2$	$O_5(OH)_4$	Great
Cronstedtite	$(Fe^{III}Fe^{II}_2)$	$(Fe^{III}Si)$	$O_5(OH)_4$	Great
Chrysotile	(Mg_3)	(Si_2)	$O_5(OH)_4$	Lattice limited in one or two dimensions
Antigorite	(Mg_3)	(Si_2)	$O_5(OH)_4$	Lattice limited in one or two dimensions
	Two Kinds of Layers—Uncharged			
Hydrated halloysite	(Al_2)	(Si_2) $(H_2O)_4$	$O_5(OH)_4$	Great—ordered sequence of types of layers
Anauxite	(Al_2)	(Si_2) (Si_4)	$O_5(OH)_4$ O_8	Considerable—irregular sequence of types of layers

ture, particularly the peculiar diffuseness of reflections from planes with the k index other than zero. Warren and K. W. Hering[10] now have apparently found the correct structure, which is simply that of kaolinite with 3 Mg ions substituted for 2 Al ions. Pauling[11] had pointed out that such substitution would be expected so to distort

[9] "The Structure of Chrysotile $H_4Mg_3Si_2O_9$," *Zeitschr. Krist.*, Vol. LXXVI (1930), pp. 201–10.

[10] "The Random Structure of Chrysotile Asbestos," *Phys. Rev.*, Vol. LIX (1941), p. 925.

[11] *Op. cit.*

the lattice, owing to the greater size of the Mg^{++} ion, as to render it unstable. Actually, this strain seems rather to restrict the width of a layer to a few units of structure, say, 30–100 A as shown by electron microscope photographs.[12] Growth along the plate, however, is still permitted; in other words, the strain is taken up in one direction. Chrysotile is thus considered to be an aggregate of kaolin-like plates perhaps only one or a few layers thick. The fibrous character is due to the extreme extension of the plates in one direction. Other clay minerals probably also will be found to develop as fibers under some conditions.

A possible structure has not yet been advanced for antigorite, and caution should be exercised in discussing it. Gruner[13] has shown that chrysotile and antigorite have powder-diffraction patterns that do not appear to be similar. Inspection of his data, however, indicates that the underlying layer structures are possibly the same and that antigorite might differ from chrysotile only in the type of lattice limitation. The $Mg_3Si_2O_5(OH)_4$ kaolin-type layers of antigorite might be more nearly equidimensional and somewhat broader than those of chrysotile. In other words, the strain caused by the presence of Mg^{++} ions would be isotropically distributed in a layer—a condition that could arise from a different rate of formation. Limitation of length would be more likely to permit several layers to be superimposed as in the kaolin minerals. We thus can have the following series: (1) nacrite, lattice not limited; (2) chrysotile, lattice limited in two dimensions, width of layers and their number; (3) antigorite, lattice limited in two dimensions, width and length of layers. Optical properties are determined by the lattice limitations, and thus antigorite and chrysotile could readily have different optic signs.

Hydrated halloysite requires some further discussion. M. Mehmel's[14] structure, described by Dr. Grim, is wrong, since it is in direct conflict with diffraction data, which, however, are not sufficiently extensive to check all other possible structures. Dr. J. Hoskins, in

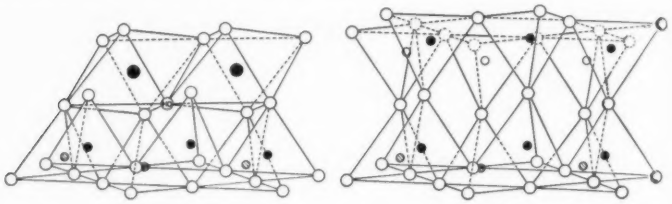
[12] H. O. Muller and E. Ruska, "An Electron Microscope for 220 Kv. Voltage," *Kolloid. Zeitschr.*, Vol. XCV (1941), pp. 21–25.

[13] "Notes on the Structures of Serpentines," *Amer. Min.*, Vol. XXII (1937), pp. 97–103.

[14] "On the Structure of Halloysite and Metahalloysite," *Zeitschr. Krist.*, Vol. XC (1935), pp. 35–43.

private communication, has raised a question about the water content of the mineral dried at 100°. We have checked two samples and find that both contain 14 per cent water, as would be required by the formula $Al_2O_3 2SiO_2 \cdot 2H_2O$ for the air-dried material.

Gruner[15] and the author[16] have both advanced suggestions to explain how the silica to alumina ratio in anauxite can be almost 3 to 1. He showed that my suggestion of raising the SiO_2 to Al_2O_3 ratio by leaving out alumina was wrong. His alternative method of replacing alumina by silicon is not structurally convincing. The correct ex-



a *b*

FIG. 2.—(*a*) Atomic arrangement in a layer of the type present in kaolin minerals. Open circles represent oxygen and (OH) ions, the larger black circles Al ions, and the smaller black and shaded circles Si ions. (*b*) Atomic arrangement in a silica layer of anauxite, the atomic designations being the same as for Figure 2, *a*.

planation seems to be that excess silica is present in the kaolin lattice as neutral silica layers with the composition SiO_2, or $4SiO_2 \cdot H_2O$, following kaolin layers in irregular sequence. The silica layers (Fig. 2) are double sheets formed by joining two silica sheets of the type present in other silicate-layer minerals. This type of layer occupies closely the same space as a usual kaolin layer. Anauxite is found only as relatively large crystals formed as an alteration product from minerals that can supply chains (pyroxenes) or sheets (micas) of silica tetrahedra.[17]

[15] "The Crystal Structure of Kaolinite," *Zeitschr. Krist.*, Vol. LXXXIII (1932), pp. 75–88; "Densities and Structural Relationships of Kaolinites and Anauxites," *Amer. Min.*, Vol. XXII (1937), pp. 855–60.

[16] "Concerning the Crystal Structure of Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and the Composition of Anauxite," *Zeitschr. Krist.*, Vol. XCV (1936), pp. 247–52.

[17] V. T. Allen, "Anauxite from the Ione Formation of California," *Amer. Min.*, Vol. XIII (1928), pp. 145–52; W. F. Foshag and C. S. Ross, "Anauxite, a Mineral Species, Based on Material from Bilin, Czechoslovakia," *Amer. Min.*, Vol. XIII (1928), pp. 153–55.

Finally, it should be pointed out that the slight amount of possible isomorphous replacement in the kaolin minerals limits the departure of the lattice from neutrality and thus restricts the amount of external exchangeable cations. This restricted base exchange exhibited by kaolinite and halloysite is probably an important factor limiting their particle size.

TALC AND MICA-LIKE MINERALS

Pyrophyllite, talc, and hydromica have similar types of layers as shown in Table 2. The most significant features of pyrophyllite and talc are their limited base-exchange capacity, their slight amount of isomorphous replacement, and their possibly large crystal-size.

TABLE 2

SILICATE-LAYER MINERALS HAVING OXYGEN IONS IN BOTH SURFACES

(Single Kind of Layer—Uncharged)

MINERAL	COMPOSITION AND CO-ORDINATION			LACK OF ORDER IN THE STACKING OF LAYERS
	Octahedral	Tetrahedral		
Pyrophyllite	(Al_2)	(Si_4)	$O_{10}(OH)_2$	Slight
Talc	(Mg_3)	(Si_4)	$O_{10}(OH)_2$	Slight
Hydromica	(Al_{2-33})	$(AlSi_3)$	$O_{10}(OH)_2$	Unknown

These properties are not unrelated. An important feature of a large crystal is that every element must fit perfectly upon every other element, and this requires the composition to be uniform throughout or to vary gradually. It is probably the large crystal-size that limits isomorphous replacement in pyrophyllite and talc as compared with montmorillonites. These properties apparently result from the minerals' being formed by hydrothermal processes, often without a liquid phase being present. Equivalent conditions in the presence of solutions will rather give montmorillonites and micas.

Hydromica, which was first described by S. L. Galpin in 1912[18] and later by Ross and Kerr,[19] is a mineral of peculiar interest in this group, since its SiO_2 to Al_2O_3 ratio is the same as that of kaolinite. It

[18] "Studies on Flint Clays and Their Associates," *Trans. Amer. Ceramic Soc.*, Vol. XIV (1912), pp. 301–46.

[19] *Op. cit.*

has the optical characteristics and water content of a mica or pyrophyllite, while having a structure similar to pyrophyllite and a silica and alumina content similar to kaolin minerals.

Attention is now directed to Table 3, in which some characteristics of mica-like minerals are presented. A. N. Winchell's[20] discovery of the distinct octophyllite and heptaphyllite series is most funda-

TABLE 3

MICA-LIKE, SILICATE-LAYER MINERALS

(Single Kind of Layer—Charged)

Mineral	Composition and Co-ordination		Lack of Order in the Stacking of Layers
	Octahedral	Tetrahedral	
	Octophyllite		
Phlogopite	$(Mg)_3$	$(AlSi_3)\ O_{10}(OH)_2$ 1.00K	Polymorphic with various degrees of order
Pholidolite	$(Mg)_3$	$(Al_{0.5}Si_{3.5})\ O_{10}(OH)_2$ 0.50K	
	Heptaphyllite		
Muscovite	(Al_2)	$(AlSo_3)\ O_{10}(OH)_2$ 1.00K	None
Bravaisite	$(A^{\cdot}{}_{1.76}Mg_{.36})$	$(Al_{0.60}Si_{3.40})O_{10}\ (OH)_2$ 0.60K	
Illite	.....	.....	
Celadonite	$(Fe^{III}_{1.00}Fe^{II}_{.25}Mg_{.75})$	$(Si_4)\ O_{10}(OH)_2$ 1.00K	

mental to understanding the micas and those mica-like substances in which all the positions that can be occupied by alkali or alkaline earth ions are not filled. Muscovite is typical of the heptaphyllite micas in which two-thirds of the positions having octahedral co-ordination with respect to oxygen are filled. It does not exhibit polymorphism, because of distortion of the silicate layers from highly symmetrical configurations—a condition that need not be true for

[20] "Studies in the Mica Group," *Amer. Jour. Sci.*, Vol. IX (5th ser., 1925), pp. 309–27, 415–30.

other heptaphyllite micas. The degraded mica-like materials, which, of course, need not be derived from micas, that Dr. Grim has described as "illites," are generally heptaphyllite micas, as he has mentioned. I have used the name "hydrous mica" for these minerals, but "bravaisite"[21] would follow the customary mineralogical practice. Celadonite is an interesting mica of the heptaphyllite type,[22] being one that is essentially free of aluminum and containing chiefly ferric and ferrous iron in octahedral co-ordination.

Phlogopite, biotite, and polylithionite are characteristic octophyllite micas,[23] exhibiting only limited solid solution with heptaphyllite ones. They are highly polymorphic, and the various forms differ as distinctly in their optical properties as do the kaolin minerals. Here we desire to call attention to pholidolite, taken from the pages of Dana,[24] which might be the degraded octophyllite mica equivalent of the heptaphyllite bravaisite or illite.

BASE EXCHANGE AND MINERALS OF THE MONTMORILLONITE GROUP

Some characteristics of base exchange in the clay minerals should be pointed out before discussing the constitutions of the montmorillonite group of clay minerals. Base exchange very likely is determined by two competing factors maintaining electrical neutrality of a particular layer. One of these is internal compensation of charge causing the appearance of more than 2 ions in octahedral co-ordination in the heptaphyllite-layer silicate minerals. Internal compensation is also effected by substitution of silicon by aluminum. The internal compensation in a layer apparently leaves the lattice negative by about one-third of an equivalent charge for each 12 oxygen *plus* hydroxyl ions of montmorillonites. This is balanced by the second factor, which is compensation of charge by cations external to a layer, the exchangeable ones.

[21] E. Mallard, "On Bravaisite, a New Mineral Substance," *Bull. Soc. Min. France* (1878), pp. 5–8.

[22] S. B. Hendricks and C. S. Ross, "Chemical Composition and Genesis of Glauconite and Celadonite," *Amer. Min.*, Vol. XXVI (1942), pp. 683–708.

[23] S. B. Hendricks, "Polymorphism . . . . ," *op. cit.*

[24] E. S. Dana, *A System of Mineralogy* (6th ed.; New York: John Wiley & Sons, 1914), p. 684.

The 102 analyses of the montmorillonite group of minerals obtained by Dr. Ross permit recognition of certain end-members, as shown in Table 4, and the types of substitution giving rise to their base exchange. Moreover, they permit some delineation of the ex-

TABLE 4

THE MONTMORILLONITE GROUP OF CLAY MINERALS

Mineral	Composition and Co-ordination		
	Octohedral	Tetrahedral	
	Heptaphyllite		
Montmorillonite	$(Al_{1.67}Mg_{.33})$ $\downarrow$ $Na_{0.33}$	(Si_4)	$O_{10}(OH)_2$
Beidellite	$(Al_{2.17})$	$(Al_{.83}Si_{3.17})$ $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$
Aluminian Nontronite	$(Fe^{III}_{2.17})$	$(Al_{.83}Si_{3.17})$ $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$
Nontronite	$(Fe^{III}_{2.00})$	$(Al_{0.33}Si_{3.67})$ $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$
	Octophyllite		
Hectorite	$(Mg_{2.67})$	$(Li_{0.33})$ (Si_4) $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$
Saponite	(Mg_3)	$(Al_{0.33}$ $Si_{3.67})$ $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$
Aluminian saponite	$(Mg_{2.67}Al_{.33})$	$(Al_{0.67}$ $Si_{3.33})$ $\downarrow$ $Na_{0.33}$	$O_{10}(OH)_2$

tent and kind of solid solution. The peculiar properties of montmorillonite seem to be due to the types of isomorphous replacements that so distort silicate layers as to prevent multiple stacking of layers and thus lead to large surfaces on which exchangeable ions are located. Unfortunately, the various analyses upon which the following dis-

cussion is based have not been published and probably will not be published in the immediate future.

Montmorillonite without aluminum in tetrahedral co-ordination can best be represented by the formula,

$$(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$$
$$\downarrow$$
$$Na_{0.33}\ .$$

Here the arrow indicates that the external exchangeable ion is essentially a result of incomplete charge in the positions having octahedral co-ordination. The formula is not exactly correct, since the number of ions in octahedral co-ordination usually slightly exceeds 2.00. It is selected because it gives a reasonable approach to a somewhat rational formula and does not differ greatly from results of some analyses.

The maximum amount of aluminum observed to have tetrahedral co-ordination in the analyzed samples is 0.83, leading to the formula

$$(Al_{2.17})(Al_{0.83}Si_{3.17})O_{10}(OH)_2$$
$$\downarrow$$
$$Na_{0.33}\ .$$

This is the formula that can be assigned to beidellite, which may be taken as an end-member of the aluminum-magnesium-montmorillonite series. Its base exchange is due to substitution of aluminum for silicon in tetrahedral co-ordination. However, this substitution is more than sufficient to compensate for the exchangeable base, and it is partially neutralized by increased charge in octahedral co-ordination positions. The maximum amount of aluminum observed to have octahedral co-ordination is 2.17 ions for every 12 negative ions (10 oxygen and 2 hydroxyl).

Magnesium is an essential constituent of the montmorillonite end of the series, but it is negligible or very low in amount as the beidellite end of the series is approached. Ferric iron can be substituted for aluminum in octahedral co-ordination throughout the montmorillonite-beidellite series, which is in sharp contrast with pyrophyllite. Possible end-members for these iron substitutions are nontronite and aluminian nontronite, which are essentially free of magnesium. Iron beidellite is realized as a naturally occurring compound, but analyzed

nontronites are never entirely free of aluminum, and minerals have not been found in which the number of ions in octahedral co-ordination fall significantly below 2.

The four minerals—montmorillonite, beidellite, nontronite, and aluminian nontronite—explain the compositions of the heptaphyllite members of the montmorillonite series. However, there are also octaphyllite members, which show only limited formation of solid solutions with the heptaphyllite members. These are a clay from Hector, California—saponite and aluminian saponite. The Hector clay, which was first described by W. F. Foshag and A. O. Woodford,[25] is of particular interest, since it apparently owes its

TABLE 5

NUMBER OF IONS HAVING OCTAHEDRAL CO-ORDINATION IN THE LAYER MINERALS FOR 12 (O+OH) IONS

Mineral and Number of Ions	Type of Replacement	Mineral and Number of Ions
Muscovite (2.0–2.1)	$2Al \longleftrightarrow 3Mg$	Phlogopite (2.9–3.0)
Muscovite (2.0–2.5)	$2Al \longleftrightarrow Li_2Al$ $Al \longleftrightarrow Si$	Lepidolite (2.7–3.0)
Pyrophyllite (2.0–2.05)	$2Al \longleftrightarrow 3Mg$	Talc (2.95–3.0)
Bravaisite (illite) (2.0–2.2)	$2Al \longleftrightarrow 3Mg$	Pholidolite (2.9–3.0)
Montmorillonite (2.0–2.2)	$Al_{1.67}Mg_{0.33} \longleftrightarrow Mg_{2.67}Li_{0.33}$	Hector clay (2.9–3.0)
Kaolinite (2.0–2.02)	$2Al \longleftrightarrow 3Mg$	Antigorite (2.98–3.0)

base-exchange capacity to substitution of lithium for magnesium in octahedral co-ordination. Very little aluminum is present, so that substitution of aluminum for silicon cannot take place. It is also the only mineral of this group that has been observed to contain appreciable fluorine substituting for hydroxyl. Saponite and aluminum saponite both seem to owe their base exchange to substitution of aluminum for silicon in tetrahedral co-ordination. Saponite, however, is free of aluminum in octahedral co-ordination, these positions being completely filled by magnesium. The saponite-aluminian saponite series is one having the substitution MgSi→AlAl.

A summary of the estimated extent of solid solution depending upon octahedral co-ordination for minerals having silicate-layer lattices is shown in Table 5. In none does there seem to be a complete

[25] "Bentonitic Magnesian Clay-Mineral from California," *Amer. Min.*, Vol. XXI (1936), pp. 238–44.

solid-solution series—muscovite-lepidolite apparently approaching it most closely. A similar condition also probably holds for the chlorites, where the octophyllite member is the mineral rumpfite, which is tucked away in an obscure corner of Dana.[26]

Finally, in Table 6, estimates for the order of magnitude of the particle dimensions for the various minerals are listed. Reasons for these estimates have been given earlier, but several might be repeated for the sake of clarity. Crystals of anauxite are large, since they utilize large sheets or chains of silica tetrahedra from coarsely crystalline silicates. Nacrite forms large crystals, since it is the most ordered kaolin mineral, probably forming extremely slowly and at an elevated temperature. Chrysotile and antigorite owe their characteristic particle-size to lattice limitation produced by strain in the

TABLE 6

ORDER OF PARTICLE DIMENSIONS OF THE SILICATE-LAYER MINERALS IN CENTIMETER

Anauxite	10^{-1}	Antigorite	10^{-5}–10^{-6}
Nacrite	10^{-1}	Micas	1.0
Dickite	10^{-2}–10^{-3}	Hydrous micas	10^{-4}–10^{-5}
Kaolinite	10^{-4}–10^{-5}	Pyrophyllite	1×10^{-1}–1×10^{-3}
Halloysite	10^{-5}	Talc	10–10^{-3}
Chrysotile	10×10^{-7}	Montmorillonites	10^{-5}–10^{-6}

lattice, accompanying presence of magnesium in octahedral co-ordination. The small particle-size of montmorillonite is determined by the substitutions in the lattice, which so distort the individual layers as to limit their stacking and which give rise to interlayer ions that permit surface hydration in aqueous systems. The extensive isomorphous replacements in montmorillonite as compared with pyrophyllite are possible, since the lattice is essentially only a few layers thick and the crystals are small. Montmorillonites and antigorite are thus rather comparable.

In concluding, it might be well to emphasize that a knowledge of crystal structures alone will not adequately serve to explain all physical properties of clay minerals. Tensile strengths, Atterberg limits, bonding strengths, shrinkage, and similar properties are only indirectly dependent upon structure, and that perhaps insensitively.

[26] *Op. cit.*

Very little progress has yet been made in understanding structure-sensitive properties such as tensile strength of crystals. Some of the explanations advanced here are by no means fully demonstrated, but that is always true in a borderland. The country beyond the frontier is fertile, but much hard work remains to be done on its trails.

SUMMARY

Factors are discussed that determine the manner in which silicate layers of clay minerals are superimposed. Relationships are shown between the kaolin minerals and chrysotile, antigorite, anauxite, and cronstedtite. Pholidolite is possibly the hydrous octaphyllite-type mica, while bravaisite or illite is the hydrous heptaphyllite mica. Formulas derived from the montmorillonite-type clay mineral analyses collected by Ross are summarized in Table 4. These formulas show the nature of the isomorphous replacements that determine the base-exchange capacities of the montmorillonite group of clay minerals.

ACKNOWLEDGMENTS.—For many years I have enjoyed free exchange of ideas with many investigators on clays and have been associated with Dr. Clarence Ross of the United States Geological Survey. Much of the information that I have presented on the montmorillonite group of minerals comes from his exhaustive work that is yet unpublished. Concepts, right or wrong, untested or demonstrated, on chrysotile and antigorite come from discussions with Professor B. E. Warren of the Massachusetts Institute of Technology.

APPLICATIONS OF MODERN CLAY RESEARCHES IN CONSTRUCTION ENGINEERING[1]

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ABSTRACT

The settlement of buildings and the stability of dams, fills, and cuts are governed by mechanical properties such as compressibility, permeability, and resistance to shear. In this field the impacts of modern clay researches have been mainly explanations for empirically found and mathematically formulated rules.

In highway engineering, the soils considered are within the zone of daily and seasonal moisture and temperature changes. Therefore, their properties must be known as functions of these variables. The constants of these functions are determined mainly by the crystal structure, the gross chemical composition, and the type and amount of exchangeable ions of the clay.

Base exchange has been employed in construction to alter undesirable soil properties (Treasure Island, San Francisco). The ease with which a roadbed is stabilized by means of bitumen or Portland cement depends upon the SiO_2-R_2O_3 ratio and on the type and amount of exchangeable ions of the clay fraction.

INTRODUCTION

Clausewitz makes the statement that one who is engaged in war must bring nothing from his books but the education of his mind. If he attempts to use ready and fixed ideas, which are not inspired by the impact of the moment, which he has not created out of his own flesh and blood, then the current of events will destroy his construction before it is finished.

Soil engineering is a war against the forces of nature—a war in which nature has the added advantage of determining the rules of combat, while the engineer might at best be free to choose the battlefield. Similarly, as in the war of men against men, so in the war of soil engineering against nature, preconceived ideas are as treacherous as fifth columns; and the advantage will be on the side of one whose mind is schooled and cleansed by many disciplines and is replete with knowledge of the tools and techniques of the many phases of human science which might touch the field of his endeavor. Such tools and techniques are presented to the soils engineer by those who are engaged in modern clay researches. The engineer who knows how to

[1] Prepared by invitation for the Fiftieth Anniversary Program of the University of Chicago, September, 1941.

use these wisely in the solution of some of his problems has a great advantage over one who is ignorant of their existence. However, ignorance of these new tools is often far better than their unjudicious use. Like the soldier, the engineer must bring nothing from his books but the education of his mind.

SOIL USES IN CONSTRUCTION ENGINEERING

As man cannot get away from his shadow, so the civil engineer cannot get away from soil. True, if bedrock is close, the engineer may found his structure on it; however, in the removal of the surface material or the driving of the piles he has a soil problem on hand. In most construction cases the civil engineer must rely on the soil to carry the structure and service loads. The soil in such cases determines the maximum allowable loads and the most suitable foundation to be employed.

Engineering differs from pure science mainly through the entrance of the economic requirement. A structure, besides being scientifically sound, must be economically feasible. Many very important structures, such as levees, earth dams, and highway fills, are possible only because of the availability of soil as building material. Since the engineering properties of soils vary from location to location, the vagaries and inconsistencies of the material must be overcome by good engineering.

A relationship of special intimacy exists between soils and highway pavements. A well-designed pavement is tailor-made for the soil *in situ*. Like a good suit or an armor, the pavement may have to be patted or plated to bring the condition of the whole up to a certain standard of appearance and service. However, like the knight in the armor, it is the soil-body with its strength and weaknesses which decides the final issue.

Age-honored is the use of soil as a building material for low-cost housing. Sun-baked bricks carried the tower of Babylon to staggering heights, and an architecture of quaint charm grew up in Europe based on the tamping of earth walls in the interspaces of the roof-supporting framework. Of equal cultural and engineering interest are the adobe constructions of our own aborigines. Not all soils are qualified for such usage. However, a large number can be improved

by addition of small amounts of extraneous materials, such as straw, used in the time of Joseph.[2] Application of small amounts of bitumen, Portland cement, and other low-cost materials has been developed in recent years to such an extent that the resulting soil systems have become standard materials in the construction of highway and airfield bases and surfaces.

The great builders of the past centuries must have possessed an intimate understanding of soils and of the problems they present to the engineer. However, with the advent of our modern age and with the destruction of the time-honored guild system of the builders, the stream of available knowledge dispersed into smaller and smaller rivulets, many of which were lost. The rising science of mechanics, so splendidly perfected by Newton, had to be called upon for help in the new construction problems, although it was not easy to establish the right contact between the single-mindedness of abstract science and multivaried reality.

We are fortunate that in our time a renaissance has taken place in soil engineering. Professor Karl Terzaghi, by his excellent and untiring work, carved out a new bed, in which all the rivulets of soil knowledge may again flow together to form the great stream of soil mechanics.[3]

ENGINEERING USAGE OF THE TERM "SOIL"

In engineering usage the term "soil" embraces a wide variety of materials ranging from the boulders of Passamaquoddy to particles revealed only under the ultramicroscope. For rough distinction these materials have been divided into cohesionless and cohesive classes. Since clay researches bear only on the cohesive class, I shall not be able to bring to your attention the important work which has been done on the properties of noncohesive soils by the great soil laboratories of Massachusetts Institute of Technology, Harvard,

[2] There exist cogent reasons to assume that the use of straw was not so much for the purpose of fibrous reinforcement as it was based on the effect of the tannin contained in the straw on the physical properties of the clay (see E. G. Acheson, "Deflocculated Graphite," *Colloid Chem.*, Vol. III [1926], p. 547).

[3] See "The Study of Earths—an American Tradition," *Civil Engineering*, Vol. XI (August, 1941); "The Early Antecedents of Soil Mechanics" and "Scientific Methods and Terminology in Studying Earths," *ibid.*, October, 1941.

and the army engineers. However, no general paper bearing on soil mechanics could be even partly complete without mention of the contributions from these great institutions. Because of the limitation stated, I should like to use in the remainder of the paper the term "soil" as restricted to a cohesive soil material. The physical properties of such a material are determined to the greatest extent by the amount and type of clay present.

THE TWO MAJOR GROUPS OF ENGINEERING SOIL PROBLEMS

A logical discussion of fundamental problems in soil engineering is greatly facilitated by their division into two major groups. One group is associated by the fact that it is concerned with soil masses which, because of either their dimensions or their location, are not subject to the influence of frequent moisture and temperature changes. To this group belong the settlement analyses for buildings and structures founded on compressible soil strata and the analyses for the inherent stability of dams, fills, cuts, levees, and retaining walls and other similar structures. The second group is concerned with the behavior of soil-surface layers of limited thickness, which are within the zone of daily and seasonal moisture and temperature changes. The obvious difference between the problems falling in the two groups is the static nature of those in the first and the dynamic character of those in the second. Problems in highway and airport construction make up the bulk of the second group.

SOIL SYSTEMS OUT OF REACH OF TEMPERATURE AND MOISTURE FLUCTUATIONS

Professor Terzaghi has proposed and developed the general theory covering the settlement of buildings caused by the compression of a water-saturated soil layer.[4] In order to estimate the probable settlement which a structure will suffer, it is necessary to know (1) the law of stress distribution which holds for the soil under consideration;[5] (2) the compressibility of the soil, which determines the total

[4] "Modern Conceptions concerning Foundation Engineering," *Jour. Boston Soc. Civil Engineers*, Vol. XII (December, 1925) (reprinted Contrib. to *Soil. Mech.* [1940], pp. 1–44).

[5] J. V. Boussinesq, *Application des potentiels à l'étude de l'équilibre et du movement des solides élastiques* (Paris: Cauthier-Villars, 1895); and O. K. Froehlich, *Druckverteilung im Baugrund* (Wien: Julius Springer, 1934), p. 24.

settlement to be expected; (3) the permeability of the soil, which determines the rate of settlement, since volume-change may occur only by loss of the pore water; and (4) shear and plastic-flow properties which may be responsible for secondary consolidation. (This latter phenomenon is only now beginning to find adequate treatment.)[6]

The physical characteristics of natural soil bodies are functionally connected with the properties of their constituent particles. These constituents are normally gravel, sand, silt, clay, water, air, and organic matter. The clay is therefore only one of many components of the system, and obviously its properties cannot always be determinant. Also, soil bodies are structures formed of the constituents by the dynamics of climatic forces. Consequently, the properties of a soil in its natural condition are only as susceptible to prediction from the amount and properties of its constituents as the character of house or hall can be predicted from a pile of material that goes into its construction. Impressive examples of the importance of structure in soil have been given by Arthur Casagrande.[7] For these reasons the four soil properties named above must be determined by actual test on representative samples.[8] The situation described makes it obvious that the contributions from modern clay researches to this phase of soil mechanics are so far mainly explanatory, although other definitely practical applications are already on record. Terzaghi[9] has given a very interesting model demonstration of the influence of plate-shaped particles on the swelling and compressive behavior of soil systems. The very impressive work by K. von Endell, Ralph E.

[6] Donald W. Taylor and Wilfred Merchant, "A Theory of Clay Consolidation Accounting for Secondary Compression," *Jour. Math. and Physics.*, Vol. XIX (July, 1940), pp. 167–85.

[7] "Structure of Clay and Its Importance in Foundation Engineering," *Jour. Boston Soc. Civil Engineers* (April, 1932) (reprinted contrib. to *Soil Mech.* [1940], pp. 72–126).

[8] M. J. Hvorslev, "Report to the Committee on Sampling and Testing," Soil Mechanics and Foundation Division, American Society of Civil Engineers, 1940, *Supplement to Purdue Conference, Purdue University, 1940;* and H. A. Mohr, "Exploration of Soil Conditions and Sampling Operations," Harvard University, February, 1940 (*Soil Mech.*, Ser. No. 9).

[9] "The Influence of Elasticity and Permeability on the Swelling of Two-Phase Systems," *Colloid Chem.*, Vol. III (1931), pp. 65–88.

Grim, Sterling B. Hendricks, and Walter P. Kelley, and their schools on the crystal structure of the clay minerals[10] induced the author[11] to apply J. Ducleaux's[12] concept of the kinetic-electrostatic equilibrium of the swarm ions to the case of a planar electric field as represented by the scalelike clay particles. Until the time when quantitative soil-water relationships can be predicted on the basis of thoroughly established crystal structures, this qualitative picture appears to be adequate for purposes of construction engineering. On the basis of the combined concepts of Terzaghi and Winterkorn a theory can be formulated which agrees closely with observed load-compression relationships of water-saturated cohesive soils.

APPLICATION OF MODERN CLAY RESEARCHES

The findings of modern clay researches which are of the greatest interest to construction engineers may be summarized as follows (soil structure being left out of consideration).

1. The crystal structure of the clay minerals and, especially, the chemical composition of their surfaces determine their own affinity for water and also dominate the water relationships of cohesive soils; the type and amount of exchangeable cations play an exceedingly important role in this connection.[13]

2. The same fundamental factors govern mechanical soil properties, such as shear resistance, permeability, and plastic flow.[14]

3. As a consequence, the water affinity (resulting in volume changes), the shear resistance, and the permeability of soil systems may be radically altered by introduction of different exchange ions.

[10] In order to avoid duplication, reference is made to the thorough coverage of these contributions in "Modern Concepts of Clay Materials" by Dr. Ralph E. Grim (see p. 225).

[11] "Surface Behaviour of Bentonites and Clays," *Soil Sci.*, Vol. XLI (1936), p. 25; and "Physico-chemical Testing of Soils and Application of the Results in Practice," *Proc. 20th Annual Meeting Highway Res. Board* (December, 1940), pp. 798–806.

[12] "The Pressure of Colloidal Solutions," *Colloid Chem.*, Vol. I (1930), p. 515.

[13] Winterkorn, "The Application of Base Exchange and Soil Physics to Problems of Highway Construction," *Proc. Soil. Sci. Soc. Amer.*, Vol. I (1937), pp. 93–99; "Surface-Chemical Factors Influencing the Engineering Properties of Soils," *Proc. Highway Res. Board*, Vol. XVI (1936).

[14] John D. Sullivan, "Physico-chemical Control of Properties of Clay," *Trans. Electrochem. Soc.*, Vol. LXXV (1939), pp. 71–97.

USES OF Na-CLAY

The very impressive ionic effects, especially those of the Na-ion, suggest advantageous use of cations to impart special properties to soils employed in construction engineering. Unfortunately, the large soil masses which are usually involved and the mechanical problem of admixing the chemicals have not yet permitted the engineer to take full advantage of the new knowledge. So far use has been made mainly of the Na-ion effect to decrease the permeability of soil to a minimum. A classical example of good engineering has been supplied by the engineer responsible for the construction of the fresh-water lake on Treasure Island in San Francisco Bay. The bottom of the 7-acre lagoon had been covered with a 10-inch compacted clay lining to prevent seepage loss. However, a loss of 1 inch of water per day was experienced—an amount which threatened to prohibit the maintaining of the lagoon. The problem was solved practically by filling the lake with saline water from the bay, which resulted in changing the relatively pervious natural soil into Na-soil. The saline water was then removed, and the lagoon was filled with fresh water. After the excess electrolytes had been washed out from the clay layer, it assumed the low permeability of a true Na-soil. As a consequence, the loss of water per day was reduced from 1 inch to 0.1 inch.[15] A similar use of Na-soil in a hydraulic fill dam had previously been reported from Hawaii.[16]

It would appear from these examples that greater use could be made in construction engineering of the properties of Na-soils. For instance, soil blankets of low permeability can thus be prepared at reasonable cost on the upstream side of dams, or the cores of earth dams can be made more impervious by Na-ion treatment. Recently, the writer has successfully employed concentrated NaCl solutions for tracing a leakage in the soil dam of a city water reservoir, where dyeing would have been objectionable. In this case the hoped-for

[15] Charles H. Lee, "Sealing the Lagoon Lining at Treasure Island with Salt," *Proc. Amer. Soc. Civil Engineers*, February, 1940, pp. 247–63.

[16] J. B. Cox, "Construction Control on Hawaiian Hydraulic Fill Dam Based on Physical Chemistry," *Hydraulic Engineering*, Vol. V, No. 12 (1929), pp. 16–20 and 42; see also "Collapsed Alexander Dam a Notable Structure," *Engineering News Record*, April 24, 1930.

additional effect of stopping the leak by the swelling of the resulting Na-soil was also obtained.

A clay material which possesses an outstandingly great water-binding ability and consequently a very low permeability for water is bentonite. Because of these remarkable properties it is employed in construction engineering in many cases in which a porous medium is to be made watertight. Used in injections, especially in combination with grouting materials, it has developed into a tool of utmost importance for the construction and maintenance engineer.[17]

THE IMPORTANCE OF SHEAR RESISTANCE

The rational design of earth dams, fills, levees, retaining walls, and similar structures involves an analysis of their inherent stability. All stability depends on the shear resistance of the materials involved. In practice the design is based on shear data obtained in the laboratory on representative soil samples which have been taken from the site of the project. The stability analysis stands or falls with the dependability of these test data.[18] It is an unfortunate fact that very little is known about the micromechanism involved in the shear of cohesive soils; and the all-important relationship between the shearing resistance of a cohesive soil and the normal pressure on the shear plane is still a book with seven seals. This book must be opened, if safer and more economical design is to be achieved. As a part of the problem, research work is being performed at the University of Missouri concerning the effect of clay composition and exchange ions on the shear resistance of cohesive soils. Data obtained so far appear to be quite promising.[19]

COHESION, FRICTION, AND PLASTICITY

The late Professor Franz Koegler has reported a simple (almost straight-line), inverse relationship between the plastic index (mois-

[17] Information concerning this material may be obtained from the American Colloid Company, Chicago, Ill.

[18] For an excellent treatment of all engineering factors involved see Donald W. Taylor, "Stability of Earth Slopes," *Jour. Boston Soc. Civil Engineers*, July, 1937 (reprinted contrib. to *Soil Mech.* [1940], pp. 337–86).

[19] Winterkorn, "Physico-chemical Testing . . . . ," *loc. cit.*

ture range in which the material exhibits plastic properties) and the angle of friction of cohesive soils. This relationship was obtained by plotting the respective properties of a large number of soil samples. Since the plastic index of a soil can be altered easily by changing the adsorbed ions, the finding of Koegler[20] would indicate that ionic substitution changes both the frictional and the cohesive properties of soil systems.

At this point it appears to be worth while to offer an idea or two concerning the plasticity of clays in addition to those which have already found excellent treatment in the paper by Dr. Grim. It is conceded by most clay experts that the plasticity is caused by the platelike shape of the clay minerals. This is a brilliant and seductive half-truth. According to Gustav Tammann,[21] the plasticity of a crystallite conglomerate is determined, among other factors, by the number of gliding-plane systems per unit volume. It should be obvious that the plate shape of the clay interferes with the free formation of gliding planes in the unlimited number of possible directions. Therefore, the platy clay particles cannot by themselves give a greater plasticity, but they are responsible for the range of moisture content within which the clay system possesses plastic properties. The reason for this latter effect lies in the special behavior of any force field connected with a plane surface as differentiated from one originating from a curved surface.[22]

Also there exists a tendency on the part of clay workers outside the field of construction engineering to overlook the importance of friction in cohesive soil systems. True, frictional effects might be small, but they are no less important than cohesional ones. The research program which is being pursued at the present time at the University of Missouri includes an experimental attack toward the understanding of the shear mechanism in cohesive soils. In view of the fast-progressing elucidation of the clay crystal structures, especially by the work of Hendricks and Kelley, the writer feels optimistic that, on the basis of their crystal models, a statistic-mechani-

[20] *Baugrund und Bauwerk* (Berlin: Verl. Wilhelm Ernst u. Sohn, 1938), p. 60.

[21] *A Textbook of Metallography* (New York: Chemical Catalog Co., 1925), p. 72.

[22] Winterkorn, "Physico-chemical Testing . . . . ," *loc. cit.*

cal analysis of the frictional characteristics of the adsorbed water layers may be possible.[23]

It is evident from the discussion offered above that any light which can be thrown on clay-water relationships by the work of the crystallographer, mineralogist, physical chemist, or any other student of clay will be of greatest importance for construction engineering. On the other hand, the observation of actual soil behavior by the engineer can be of great help in circumscribing the range of permissible extrapolations from crystallographic data, which, though exact, might be of too limited a scope to permit sweeping predictions.

SOIL DYNAMIC PROBLEMS IN HIGHWAY ENGINEERING

The engineering phases which have been touched upon so far were concerned with soil masses in which temperature and moisture variations played no significant role. As a consequence, the problems to be considered were restricted to a few physical phenomena which could be handled by static analysis once the soil properties involved were known. Little deterioration of the initial stability of such soil structures may be expected during the years following construction. Exception, of course, must be made of such damage as can arise from critical seepage conditions.

The situation is completely reversed in the case of surface- and subgrade-soil systems which are employed in highway and airport construction. Soil subgrades are usually stable during and immediately after construction of the pavement, but soon thereafter the dynamic effects of temperature and moisture variations enter the picture. Increase of the moisture content causes swelling, and decrease causes shrinkage and cracking of the soil mass. The cracks, in turn, serve as ports of entrance for the next precipitation water. At constant moisture content, increase in temperature decreases the water-holding capacity of the soil constituents and softens the soil-water system; decrease in temperature increases the water-holding capacity of the soil constituents and the viscosity of the water and makes the soil-water system more resistant to deformation. A great

[23] For the type of promising attack on this problem see J. F. Kincaid, Henry Eyring, and Allen E. Stearn, "The Theory of Absolute Reaction Rates and Its Application to Viscosity and Diffusion in the Liquid State," *Chem. Rev.*, Vol. XXVIII (April, 1941).

drop in temperature results in the freezing of the soil, which is accompanied either by a primary volume change (caused by the expansion of water in freezing under atmospheric pressure) or by a primary and secondary volume change, the latter being caused by the formation of ice lenses. The complexity of the systems under consideration will be easily visualized, especially if, to the enumerated effects, the direct influences of temperature and moisture content on the elastic properties of the multivariant solid soil constituents are added. It is as yet impossible to picture theoretically sound micromechanisms on the basis of fundamental molecular and crystal physics for these ever changing, pulsating dynamic systems. The natural forces acting in our subgrades are identical with those which have formed the soils and have given them their present characteristics. For these reasons the highway engineer has drunk lustily from the deep well of information which the science of pedology[24] has made available. As a consequence, he has learned to know and to apply such concepts as the silico-sesquioxide ratio of clays. This concept, though qualitative, has been of great benefit to the engineer.

During the last fifteen years clay researchers have developed a new and excellent tool to analyze and systematize the structure of clay minerals in the application of X-ray spectrograms. In the first enthusiasm over their success some crystallographers have become prone to underestimate the value of the older tools of the pedologist. The record of usefulness of the silico-sesquioxide ratio speaks for itself. However, with the availability of the more exact knowledge provided by the crystallographer it can be hoped that the pedologic silico-sesquioxide concept will be replaced by the concept of mineral paragenesis. The progress in this direction by Kelley and others[25] is promising. As far as the water affinity of the soil colloids is concerned, the silica and sesquioxide content of the clay cannot be neglected in the concept to come. As has been shown long ago by

[24] C. F. Marbut, "A Scheme for Soil Classification, *Proc. and Papers First Internat. Cong. Soil. Sci.*, Vol. IV (1928), pp. 1–31; and Jacob S. Joffe, *Pedology* (New Brunswick, N.J.: Rutgers University Press, 1936).

[25] W. P. Kelley, W. H. Dore, and J. B. Page, "The Colloidal Constituents of American Alkali Soils," *Soil Sci.*, Vol. LI (1941), pp. 101–24; and I. D. Sedletskii, "Paragenesis of Elements and Minerals in Colloids of Soils and Clays," *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XXX (1941), pp. 160–62.

Kossel, there exists a great difference in the character of an oxygen or hydroxyl, depending upon whether it is bound to a Si^{++++} or an Fe^{+++} or an Al^{+++} ion. Also, it must not be forgotten that in actual soils the clay minerals are often covered by noncrystalline hydroxide, oxide, and organic films, the effect of which may greatly overshadow the influence of the clay minerals on the properties of the soil *in toto*. Especially, the effect of organic matter in soil is difficult to predict or even to evaluate.[26]

From the preceding discussion it is evident that the factors responsible for soil behavior are too many and too complex to permit an exact theoretical analysis. At best we may have a general mosaic-like picture with off-colors and off-size pieces. One detail—one stone—means nothing; we must have a concept of the whole; we must have a grasp, even though it can be only qualitative, of the dynamic nature of the soil system. The greatest mistakes in soil engineering are not made by those totally ignorant of soil learning but by those who know everything about one limited phase of the picture.

THE FIGHT AGAINST THE FORCES OF NATURE

A striking example of the complexity of problems which the highway engineer continuously encounters is concerned with frost action and frost damage in soils. Progress has been made in this complex problem by the work of Stephen Taber,[27] Arthur Casagrande,[28] Gunnar Beskov,[29] Franz Koegler and others;[30] however, our knowledge of the processes going on in a freezing soil is still in a very deplorable state. It appears that only a thorough thermodynamic analysis of all the phenomena involved can bring us closer to a theoretical and practical solution of the frost problem.

[26] Winterkorn, "Physico-chemical Testing . . . . ," *op. cit.*, p. 805; and Winterkorn and George W. Eckert, "Physico-chemical Factors of Importance in Bituminous Soil Stabilization," *Proc. Assoc. Asphalt Paving Tech.*, Vol. XI (1940), pp. 204–57.

[27] "Frost Heaving," *Jour. Geol.*, Vol. XXXVII (1929); "Mechanics of Frost Heaving," Vol. XXXVIII (1930); also *Public Roads*, Vol. XI (1931).

[28] *Proc. Highway Res. Board*, Vol. XI (1931); "Frostschäden im Strassenbau," *Die Strasse* (1935).

[29] *Tjälbildningen och Tjällyftningen* (Stockholm: Sveriges Geologista Undersökning, 1935).

[30] "Beiträge zur Frostfrage," *Die Strasse*, Heft 3 (1936).

Fighting against the ever present forces of nature, the highway engineer is attempting to keep changes in consistency and volume in the subgrades at a minimum. In this great task he is aided by the knowledge which pedology and geology can supply of the formation of the particular soil under consideration. He is aided also by the Bureau of Public Roads classification of subgrade soils, which is based on their physical properties. This classification, which represents an immensely practical result of the untiring efforts of Mr. C. A. Hogentogler of the Federal Works Agency, is given in Table 1. While apparently this table contains no reference to the results of modern clay researches, the list of the outstanding soil properties under the headings of "friction," "cohesion," "expansion," "elasticity," and "capillarity," illuminates at once the great importance of the amount and structure of the clay minerals, which in cohesive soils determine these properties. The more clay knowledge an engineer possesses, the more judiciously is he enabled to employ the above-presented empirical system. If a soil falls into the A-1 group, there is little need for worry; if it falls into the other groups, it is usually desirable to make up its deficiencies by the most economical method available. Any method of treatment which assists a soil in a better performance of its role may be classed as stabilization. The system reproduced in the following has been offered as the most logical classification of highway soil-stabilization methods:[31]

1. *Mechanical stabilization.*—Effect mainly due to manipulation and compaction of the soil. This includes possible use of water and such salt solutions as are not entirely alien to the soil and which, while able to change the physical properties of the soils, do not render them fundamentally different systems.
2. *Physical stabilization.*—Preparation of graded soil mixtures by adding coarse- or fine-soil constituents. The latter do not lose their physical identity in the system and can be reclaimed by physical means such as screening, flotation, sedimentation, etc. The group includes dilution stabilization, clay-gravel, sand-clay systems, and similar ones with or without addition of salt solutions as under (1).
3. *Chemical stabilization.*—Addition of materials which, because of their own chemical character and that of the soil systems, react and form new systems from which the original components cannot be reclaimed entirely by physical

[31] Winterkorn, "Recent Developments in Soil Stabilization," *Proc. 1939 Montana Nat. Bituminous Conf.*, Vol. IV (1940), pp. 125–38.

TABLE 1*

CLASSIFICATION OF SUBGRADE SOILS ON BASIS OF PHYSICAL PROPERTIES

GROUPING	SIZE COMPOSITION (IN PERCENTAGE)					MAXIMUM DRY WEIGHT (LB./CU. FT.)	CONSISTENCY DATA			OUTSTANDING PROPERTIES	VALUE OF SOIL-BINDER MATERIAL
	General Grading	Sand	Silt	Clay	Colloids		S.L.	P.I.	L.L.		
A-1	Uniform	70–85	10–20	5–10	0–5	130+	14–20	4–8	14–25	High internal friction, high cohesion	Excellent binder, regardless of moisture condition
A-2	Lack in certain sizes	55+	Low	High	High	120–30	25+	0–15	14–35	High internal friction and high cohesion if properly graded	Good when dry, may soften when wet
A-3	Coarse	50–95	0–5	0–10	Low	110–30	.....	0	10–35	High internal friction, no cohesion	Excellent for base course, poor for surface
A-4	Lack in coarse and finest sizes	−55	30–90	10–30	Low	110–20	25+	0–16	20–40	Variable internal friction, slight cohesion, high capillarity	Rapid water absorption causes instability; poor base
A-5	Like A-4		Similar to A-4			90–100	30–50	Rarely 16+	35+	Similar to A-4 *plus* high elasticity	Similar to A-4 but more elastic; difficult to compact
A-6	Lack in coarse and intermediate sizes	Low	Medium	30+	High	100–110	8–15	16+	35+	High cohesion, high expansion	Absorbs water only if worked, then becomes mushy; cracks on drying
A-7	Like A-6		Similar to A-6			90–110	12–40	16+	35+	Similar to A-6 *plus* high elasticity	Like A-6 but has excessive volume change
A-8	Like A-6	Organic soils; peat and muck				−90	20–50	16+	45+	High expansion, high capillarity, high elasticity	Soft peat and muck, unsatisfactory

* This table is based on one published by Arthur R. Smith in *ABC's of Soil Stabilization* (Chicago: Burton Pub. Co., 1939.)

and mechanical means. Also, cementation stabilization by hydraulic and other cements.

4. *Physicochemical stabilization.*—The effectiveness of treatments falling in this group is due to both physical and surface-chemical factors which cannot be cleanly separated, while the relative importance of each of these factors may vary. A good example for this is bituminous stabilization, in which both the physical and the chemical properties of bitumen and soil play important roles. The bituminous stabilization of dune sands borders more on physical stabilization, while that of cohesive soils is governed to the greatest extent by chemical factors.

Of course, mechanical, physical, physicochemical, and chemical factors play a role in all types of soil stabilization. If a classification be established at all, it can be done only by emphasis on the predominant factor.

RECENT RESEARCH IN SOIL STABILIZATION

Research work, especially that performed during the last ten years by the Missouri State Highway Department and by the University of Missouri, has demonstrated the important bearing of structure and chemical composition of clay materials on the ease with which soil systems may be stabilized. The evidence accumulated is too bulky to be presented here; however, most of it is available in published reports.[32] Conclusions which can be drawn from this work are especially interesting, since they show that the effect of the chemistry and structure of the clay particles is more direct and more evident in stabilized soil systems than in untreated soils. In the latter, secondary effects of structure and aggregation render extremely difficult an exact prediction of the properties of a soil system from those of the clay components. These secondary effects are eliminated to a great extent in physicochemical and chemical types of stabilization, where the surface of the soil constituents reacts with materials like bitumen or Portland cement.

An extensive investigation on the physicochemical factors affecting the bituminous stabilization of cohesive soils[33] has demonstrated that the ease of stabilization depends upon the SiO_2-R_2O_3 ratio of the clay constituents, the type and amount of organic matter, and

[32] Winterkorn, "Physico-chemical Testing . . . . ," *op. cit.;* "Recent Developments . . . . ," *op. cit.;* and "Surface Behaviour of Bentonites . . . . ," *op. cit.*

[33] Winterkorn and Eckert, *op. cit.*

* This table is based on one published by Arthur R. Smith in *ABC's of Soil Stabilization* (Chicago: Burton Pub. Co., 1929.)

the type and amount of exchangeable cations which are present. Preferable are small silico-sesquioxide ratios, high-valent exchange ions, and chernozem type of organic matter.

An extensive investigation is now under way concerning the influence of the above-named factors in the stabilization of soils by means of Portland cement. Work completed so far gives indications closely parallel to those obtained for bituminous stabilization. Important differences are found, however, which are caused by the fundamental differences in the chemical nature of the reacting agents. From the work done by Harold Gibbs[34] it appears that the energy of water adsorption by the soil colloids contained in the system may attain importance in the judging of soil behavior in cement stabilization.

CONCLUSION

It has been attempted in this short paper to indicate the importance of modern clay researches for construction engineering and to give key references for those who are seriously interested in this particular field of application.

To return to the simile employed in the introduction, it is most important for the soil engineer that he adjust his perspective to the conditions of the moment, that he exploit the best available knowledge, but also that he avoid deep entanglement with any fixed and ready ideas, however alluring and seductive.

[34] "An Experimental Investigation of Soil-Chemical Effects on Soil Hardening by Means of Portland Cement" (Master's thesis, University of Missouri, 1941).

MODERN CLAY RESEARCHES IN RELATION TO AGRICULTURE[1]

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ABSTRACT

The researches on the clays are of great importance in the chemistry, physics, and genesis of soils. Formerly inorganic soil colloids were thought to be composed largely of uncombined oxides and hydroxides of silicon, iron, and aluminum, and soil clay was looked upon as being amorphous. During recent years it has been shown that clay minerals are important constituents of soil colloids generally. The phenomena of base exchange, absorption in general, and the structure and tilth of soils are all greatly influenced by the clay minerals of soils. Investigations on these subjects have already been considerably influenced by the researches on the clays. The discovery that the clay minerals are widely distributed in soils and that certain soils contain kaolinitic clay minerals, others contain montmorillonitic clay minerals, and still others contain mica-like clay minerals, has stimulated interest in the question: What are the essential conditions for the formation of the different clay minerals? The researches on the clays have served to show the close relationship between soil science and geology.

INTRODUCTION

To an important degree agriculture is based on clay. In fact, clay is one of the two most fundamentally important substances in soils. The movement of water within and through the soil and its availability to plants are greatly influenced by the clay content. The capacity of soils to hold water against the force of gravity is roughly proportional to their clay content, but the availability of the water to plants is not necessarily determined by the absolute amount of clay in the soil. Recent experiments have shown that plants may wilt considerably more quickly when grown on certain soil types than on other soils of like clay content. In such cases water seems to be attracted by the clay with unequal degrees of force. It appears to be held more strongly by the clay of certain soils than by that of others. It is possible that this is due in part, at least, to differences in the essential nature of the clay present. Clay also has a direct bearing on soil erosion. The state of dispersion of the clay particles and the stability of the clay aggregates greatly influence the erosibility of soils.

[1] Address delivered at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941.

The absorptive power of clay has peculiar importance in the field of agriculture. By virtue of this property, the loss of valuable plant nutrients by leaching is largely prevented, especially certain of those added as fertilizer. At the same time the nutrients are held by the clay in a form that is available to plants. Soil clay has long been known to possess the property of base exchange; potassium, calcium, and magnesium in soils generally and sodium in arid regions are adsorbed by clay and held in an exchangeable form. Hydrogen ions, formed in soils by the growth of plants, by the decay of organic matter, and by the life-processes of microörganisms, react with the soil, replacing the adsorbed bases of the clay and thus making them available to growing plants. Thus clay constitutes a sort of storehouse for certain elements that are important as plant nutrients.

When any of the adsorbed bases of clay are replaced by H ions, the clay tends to become acid. The intensity of the acidity—that is, the pH—is determined by the percentage saturation with H ions. Therefore, the acidity of clay soil ordinarily does not mean water-soluble acids; rather it means acid clay. We speak of "calcium clay," meaning clay whose adsorbed and, therefore, replaceable ions are largely calcium ions, and of "acid clay" meaning clay containing exchangeable H ions.

In arid regions the clay of soils often contains relatively much adsorbed sodium. Such soils are usually strongly alkaline, owing to the hydrolytic tendency of sodium clay, and at the same time the percolation of water through the soil is subnormal, owing to the fact that sodium clay tends to be deflocculated. Therefore, the reclamation of alkali soils may involve not merely the removal of excessive amounts of the soluble salts, which they commonly contain, but also the conversion of sodium clay into calcium clay, which is the desirable form.

Clay is also important in soil classification. We speak of "sandy soils," "sandy loams," and "clay loams," having reference very largely to their clay content. Clay is, indeed, an important consideration in soil classification, particularly as regards its vertical distribution in the soil profile. However, too much clay is likely to produce adverse effects on the physical properties, the tilth, and the drainage conditions of soils. The temperature relations of heavy

clay soil are likely to be unfavorable; they tend to remain cold late into the spring.

Clay, then, regulates the moisture of the soil, its base and water-supplying power, acidity, tilth, and the general physical and chemical properties. At the same time it is important in soil classification. Clay is, therefore, one of the most fundamentally important substances in the soil.

Nevertheless, it is only recently that soil scientists have begun to understand this substance. Modern researches on the clays have already contributed substantially to this understanding. Perhaps brief reference to older ideas regarding the nature of soil clay will bring this contribution into focus.

FORMER CONCEPTS OF SOIL CLAY

Although C. A. Ross[2] pointed out in 1927 that crystalline clay minerals are commonly present in soils, practically all soil scientists held, until about ten years ago, that soil clay is an amorphous substance consisting chiefly of the oxides of silicon, iron, and aluminum. It has been known for some time, however, that much, at least, of the silicon and aluminum of the so-called "clay fraction" of soils is chemically combined rather than being present as uncombined oxides. But the term "clay," as formerly used in soil literature, does not denote any specific mineral as the mineralogists use the word. It merely means finely divided inorganic material. The idea that different kinds of clay may occur in near-by soils, or even in the same soil, appears to have been foreign to the understanding of soil workers until quite recently. Toward the end of the nineteenth century the term "colloid" began to be applied to the fine-grained material of soils, but it was tacitly assumed that colloidal materials are necessarily noncrystalline, which, of course, was T. Graham's original idea.

CRYSTALLINITY OF SOIL COLLOIDS

Therefore, it is little wonder that the announcement that soil colloids contain crystalline materials should have aroused skepticism among soil scientists. In November, 1929, S. B. Hendricks and W.

[2] "The Mineralogy of Clays," *Proc. First Internat. Cong. Soil Sci.*, Vol. IV (1927), pp. 555–61.

H. Fry[3] presented a paper before a meeting of the American Soil Survey Association, and this was followed a few days later by a paper by the author[4] before the American Society of Agronomy, both of which papers announced that soil colloids contain important amounts of crystalline material. This, of course, confirmed Ross's conclusions of 1927. It is practically certain that but few of those present at those meetings had any idea as to what this would lead to.

Perhaps the greatest importance of these researches lies in the fact that they made possible the determination of the specific components of soil colloids and a better understanding of the properties of soils. The point need not be labored here that the determination of the specific substance with which the investigator is actually dealing is one of the most important steps he can take. It is basic to an understanding of the properties of that substance. Hendricks and Fry pointed out that a considerable number of soils from various parts of the United States contain clay minerals, some halloysitic and others montmorillonitic.[5] My purpose was twofold: first, to show that soil colloids, instead of being entirely amorphous, actually contain crystalline material, which in some instances is related to the bentonitic clays, and, second, that base exchange in soils appears to be related to the crystalline material present.[6] The results of these independent researches were in essential agreement.

Gradually others took up this problem, until, within the brief period of ten years, researches were being actively made on the clay minerals in soil laboratories here and there all over the world. The essentials of the conclusions drawn in 1927 by Ross[7] and more specifically applied to soil colloids in 1929 have been fully confirmed by many workers both at home and abroad. It is now well established that one or another or a mixture of the three principal classes of clay

[3] "The Results of X-Ray and Microscopical Examinations of Soil Colloids," *Bull. Amer. Soil Surv. Assoc.*, Vol. XI (1930), pp. 194–95; *Soil Sci.*, Vol. XXIX (1930), pp. 457–79.

[4] W. P. Kelley, "The Nature of the Base Exchange Material of Soils," *Jour. Amer Soc. Agron.*, Vol. XXI (1929), p. 1210.

[5] *Op. cit.*

[6] W. P. Kelley, W. H. Dore, and S. M. Brown, "The Nature of the Base-Exchange Material of Bentonite Soils and Zeolites as Revealed by Chemical Investigations and X-ray Analysis," *Soil Sci.*, Vol. XXXI (1931), pp. 25–55.

[7] *Op. cit.*

minerals is found in practically all soils. At present, researches are being made in many laboratories based primarily on the idea that soil colloids contain clay minerals and are therefore not entirely amorphous.

BASE-EXCHANGE MATERIAL IN SOILS

Previous to about ten years ago practically all soil workers had believed for more than three-quarters of a century that the important property of soils known as "base exchange" is a function of amorphous substances. The idea had gained stronghold that the exchangeable ions either are held by some vaguely defined force called "absorption" or else are chemically combined as compounds of unknown identity. However, the discovery that the different clay minerals possess base-exchange properties—in varying degrees, of course—has led to a new approach to the subject of base exchange.

Previously the amorphous synthetic product, known as "permutite," was commonly used in base-exchange experiments, and the base-exchange material of soil was referred to as being "zeolitic." "Soil zeolites" was a common expression in the soil literature, notwithstanding the fact that the untenability of the zeolite concept had been shown by several workers. Many soil workers still refer to the base-exchange material as the "zeolitic soil complex."

For a number of years certain soil workers held that, apart from humus material, base exchange in soils is due to a single substance which was designated the "base-exchange substance."[8] It is now definitely established, however, that there is no one single base-exchange substance in soils; rather, there are several such substances. These are found mainly in the so-called "clay fraction" of the soil, and among them the clay minerals play a large part. Montmorillonitic clays stand at the head of the list. This type of clay comes nearest being the base-exchange substance of soils, but other clay minerals have the property of base exchange to some extent; the mica-like clays have rather marked base-exchange power. Jacob A. Hofmann and others[9] claim that clay minerals are the only kind of

[8] E. Truog and J. A. Chucka, "The Origin, Nature, and Isolation of the Base-Exchange Compound of Soils," *Jour. Amer. Soc. Agron.*, Vol. XXII (1930), pp. 553–57.

[9] "Chemische und röntgenographische Untersuchungen über die mineralische Sorptionssubstanz in Boden," *Beihefte, Zeitschr. f. d. Vereins deutsch. chem. angewand. Chem. u. chem. Fabrik.*, Vol. XXI (1935), pp. 11–19.

inorganic substance of soils having any important base-exchange significance.

The clay minerals also have a limited amount of anion-exchange power. P. R. Stout[10] has recently shown that the exposed OH ions of kaolinite and halloysite may be exchanged for PO_4 ions, thus accounting for the marked phosphate-absorbing power of these clays. The importance of this discovery lies in the fact that certain soils known to contain kaolinitic clay have extraordinary phosphate-fixing power.

PHYSICAL PROPERTIES OF SOILS

During recent years evidence has been obtained which indicates that certain physical properties of soils, particularly those having to do with the structure of soils, are related to the kind of clay minerals present. Dr. Chia Wei Chang,[11] working in our laboratory, has shown that the peculiar condition known as the "adobe structure," which refers to the great swelling power of the soil when wet and the contraction into angular blocks when dry, is due to the presence of a relatively high percentage of montmorillonitic clay. As is well known, montmorillonitic clay swells when wet, sometimes enormously, and is much more readily dispersed than kaolinitic clay. The readiness with which montmorillonitic clay can be dispersed into particles of minute size, knowledge of which has come to light through researches on the clay minerals, has an important bearing on tillage operations. It appears that the farmer is most likely to deflocculate his soil, if it contains the montmorillonitic type of clay. By only a partial destruction of the natural granular structure of the soil, the tilth is injured, and the permeability to air and water is reduced.

THE CLAY MINERALS OF SOILS

Knowledge as to the kind of clay minerals found in soils bids fair to throw important light on soil-formation processes, that is, on soil genesis. Partly for this reason we have been engaged for some time

[10] "Alterations in the Crystal Structure of Clay Minerals as a Result of Phosphate Fixation," *Proc. Soil Sci. Soc. Amer.*, Vol. IV (1939), pp. 177–82.

[11] "An Experimental Study on the Development of Adobe Structures in Soils," *Soil Sci.*, Vol. LII (1941), pp. 213–23.

with the determination of the clay minerals of a wide variety of soils.[12] The results already obtained, together with those of other workers, have established the fact that each of the three principal types of clay minerals is widely distributed in the soils of various parts of the world. Kaolinite, montmorillonite, and mica-like clays have been found in soils of practically all types of climate, and each of them seems to have been formed from various kinds of parent-rocks. Kaolinite occurs in well-leached soils of both the humid temperate[13] and the humid tropical climates.[14] It is also found in certain California soils, where the rainfall does not exceed 10–12 inches per annum.[15] Montmorillonitic clay has been reported in certain soils from southern United States,[16] the Mississippi Valley,[17] the Great Plains section,[18] and the semiarid West;[19] also from England,[20] Hol-

[12] W. P. Kelley, A. O. Woodford, W. H. Dore, and S. M. Brown, "Comparative Study of the Colloids of a Cecil and a Susquehanna Soil Profile," *Soil Sci.*, Vol. XLVII (1939), pp. 175–93, and "The Colloidal Constituents of California Soils," *ibid.*, Vol. XLVIII (1939), pp. 201–55; W. P. Kelley, W. H. Dore, and J. B. Page, "The Colloidal Constituents of American Alkali Soils," *Soil Sci.*, Vol. LI (1941), pp. 101–24.

[13] L. T. Alexander, S. B. Hendricks, and R. A. Nelson, "Minerals Present in Soil Colloids. II. Estimation in Some Representative Soils," *Soil Sci.*, Vol. XLVIII (1939), pp. 273–79; Hendricks and Fry, *op. cit.;* Kelley *et al.*, "Comparative Study . . . . ," *op. cit.*

[14] H. J. Hardon and J. C. L. Favejee, "Qualitative X-Ray Analysis of the Clay Fraction of the Principal Soil Types of Java," *Overdruk uit Meded. v. d. Landbouwk.*, Vol. XLIII (1939), pp. 55–59; C. R. Wentworth, R. C. Wells, and V. T. Allen, "Ceramic Clay in Hawaii," *Amer. Min.*, Vol. XXV (1940), pp. 1–33.

[15] Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*

[16] Hendricks and Fry, *op. cit.;* and Kelley *et al.*, "Comparative Study . . . . ," *op. cit.*

[17] G. E. Ekblaw and R. E. Grim, "Some Geological Relations between the Constitution of Soil Materials and Highway Construction," *Ill. State Geol. Surv. Rept. No. 42* (1936), pp. 1–16; C. E. Marshall, "Layer Lattices and the Base-Exchange Clays," *Zeitschr. Krist.*, Vol. XCI (1935), pp. 433–49; E. P. Whiteside and C. E. Marshall, "Studies in the Degree of Dispersion of the Clays. III. The Two Layer Method as Applied to the Sharples Supercentrifuge," *Proc. Soil Sci. Soc. Amer.*, Vol. IV (1939), pp. 100–103.

[18] Alexander *et al.*, *op. cit.*

[19] Hendricks and Fry, *op. cit.;* Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*, and "The Colloidal Constituents of American . . . . ," *op. cit.*

[20] Marshall, *op. cit.*

land,[21] Germany,[22] Russia,[23] North Africa,[24] India,[25] the Netherlands East Indies,[26] the Philippine Islands,[27] Australia,[28] and Argentina.[29] Mica-like clay is found in certain soils of Germany,[30] Holland,[31] the Mississippi Valley,[32] and the Desert and West Coast sections of the United States.[33]

FORMATION OF CLAY MINERALS

Therefore, the distribution of the clay minerals appears not to be entirely determined by climate, and, as suggested already, each of the clay types occurs in soils derived from various kinds of geological formations. Kaolinite is found in soils derived from both granitic[34] and basaltic rocks.[35] Montmorillonite is found in soils from granitic, basic igneous, and metamorphic rocks[36] and also in certain

[21] C. H. Edelman, F. A. Van Baren, and J. C. L. Favejee, "General Discussion of the Mineralogical Composition of Clays and Qualitative X-ray Analysis of Some Dutch Clays," *Overdruk uit Meded. v. d. Landbouwk*, Vol. XLIII (1939), pp. 1–39; J. C. L. Favejee, "Qualitative X-ray Analysis of Some Dutch Soils," *Overdruk uit Meded. v. d. Landbouwk*, Vol. XLIII (1939), pp. 43–51.

[22] E. Maegdefrau and U. Hofmann, "Glimmerartige Mineralien als Tonsubstanzen," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp. 31–59.

[23] I. D. Sedletzky, "Absorbing Complex of Soil—a Paragenetic System of (Colloidal) Minerals," *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XXIII (1939), pp. 258–63.

[24] Hofmann *et al.*, *op. cit.*

[25] G. Nagelschmidt, A. D. Desai, and A. Muir, "The Minerals in the Clay Fractions of a Black Cotton Soil and a Red Earth from Hyderabad, Deccan State, India," *Jour. Agric. Sci.*, Vol. XXX (1940), pp. 639–53.

[26] Hardon and Favejee, *op. cit.*; Hofmann *et al.*, *op. cit.*

[27] Hofmann *et al.*, *op. cit.*

[28] J. S. Hoskins, "The Soil Clay Mineralogy of Some Australian Soils Developed on Granitic and Basaltic Parent Materials," *Jour. Coun. of Sci. and Indust. Res.*, Vol. XIII (1940), pp. 206–16.

[29] Hofmann *et al.*, *op. cit.*

[30] *Ibid.*

[31] Favejee, *op. cit.*; Hofmann *et al.*, *op. cit.*

[32] Alexander *et al.*, *op. cit.*; Ekblaw and Grim, *op. cit.*

[33] Alexander *et al.*, *op. cit.*; Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*, and "The Colloidal Constituents of American . . . . ," *op. cit.*

[34] Hendricks and Fry, *op. cit.*; Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*

[35] Hoskins, *op. cit.*

[36] Unpublished data.

soils derived from shales and sandstones.[37] Mica-like clay is found in soils derived from glacial deposits,[38] granite,[39] and other types of rocks.[40] Hence it is not possible at present to trace the clay minerals of soils to specific parent-rocks or to specific conditions of weathering, despite the claims of certain authorities to the contrary.

W. Noll[41] suggested, on the basis of synthesis under hydrothermal conditions, that acid conditions of weathering and intensive leaching favor the formation of kaolinite and that alkaline conditions under restricted leaching, particularly in the presence of magnesium compounds, favor the formation of montmorillonite. Later he[42] showed that montmorillonite occurs in the cavities of the basaltic Vogel Mountains of Germany, but he also noted kaolinite on basalt at other places in the same mountains.

Despite the reasonableness of Noll's hypothesis, we have thus far been unable to secure clear-cut evidence in its support. If alkaline conditions and the presence of magnesium salts favor the formation of montmorillonite, then it seems that montmorillonite would probably be found in alkali soils. Sedletzky[43] reported montmorillonite in certain alkali soils of Russia, which seems to confirm Noll's hypothesis, but we have found a number of exceptions in American alkali soils.[44] Since these soils are alluvial, it is possible that the clay was a constituent of the alluvium when laid down, rather than having been formed under the alkaline conditions which now exist in these soils. Moreover, the clay formed in the weathering of volcanic materials on the slopes of Mount Lassen is sometimes kaolinitic,

[37] Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*

[38] Ekblaw and Grim, *op. cit.;* P. F. Kerr, "Kaolinite from the Terminal Moraine of Staten Island," *Amer. Min.*, Vol. XVII (1932), pp. 29–34.

[39] Kelley *et al.*, "The Colloidal Constituents of California Soils," *op. cit.*, and "The Colloidal Constituents of American . . . . ," *op. cit.*

[40] Alexander *et al.*, *op. cit.;* Maegdefrau and Hofmann, *op. cit.;* and Wentworth *et al.*, *op. cit.*

[41] "Über die Bildungsbedingungen von Kaolin, Montmorillonit, Sericit, Pyrophyllit und Analcim.," *Min. u. Petrog. Mitt.*, Vol. XLVIII (1936), pp. 210–47.

[42] "Über das Vorkommen von Montmorillonit in einigen Zersetzungsprodukten von Basalten des westlichen Vogelsberges," *Chem. d. Erde.*, Vol. XI (1937), pp. 294–306.

[43] *Op. cit.*

[44] Kelley *et al.*, "The Colloidal Constituents of American . . . . ," *op. cit.*

but in other places it is montmorillonitic.[45] It is curious that those soils of California which have been derived from shales and sandstones commonly contain montmorillonitic clay.

For some time we have been investigating this question. The results, not yet published, have been very contradictory. For example, in certain parts of the Sierra Mountains, granitic rocks have weathered to kaolinite. On the other hand, quite recent granitic alluvium derived from these same mountains commonly contains mica-like clay. In one instance we found granitic rocks weathering to montmorillonite. Quite similar results have been obtained with soils derived from basic igneous rocks.

From the foregoing it should not be inferred that Noll's hypothesis has been definitely disproved or that any of the clay minerals can be formed by the weathering of any and all kinds of rocks or that the conditions under which the weathering takes place are of no importance in clay formation. Such conclusions would almost certainly be erroneous. Clay-mineral formation is undoubtedly a chemical process, and all known chemical processes are influenced, usually markedly, by temperature, pressure, the concentration of soluble electrolytes present, and by pH. It would indeed be singular if clay formation should prove to be an exception.

Nevertheless, the answer to the question of why montmorillonitic clay is found in certain soils, mica-like clay in others, and kaolinitic clay in still others cannot fail to be of interest to the geologist because of the light that will be thrown on the distribution of the clays. The elucidation of this question may also have practical agricultural importance because of the indication afforded concerning the essential nature of soil processes and the direction these processes are taking in soils.

In this connection it is appropriate to point out that an understanding of the origin and mode of formation of the clay minerals will probably require the study of residual weathering of known minerals under known conditions. In the case of transported soils it is frequently impossible to determine definitely how the clay minerals have originated, from what source they were derived, and under what conditions they were actually formed.

[45] Unpublished reports.

GENERAL IMPORTANCE OF CLAY MINERALS IN SOILS

The clay minerals certainly exert important influences on the physical and chemical properties of soils, and the physical effects produced by the clay of soils are tremendously important to agriculture. As pointed out already, the state of granulation of the clay and the stability of the clay aggregates largely determine the tilth, the permeability to air and water, and the erosibility of the soil. It appears quite probable that clay combines in some way with organic materials in soils and that this largely determines the size and arrangement of the clay particles and, therefore, the physical properties of the soil. The exact nature of this process and the forces involved are but little understood.

The water relations of clay, as discussed by Dr. Grim, are fundamental to an understanding of soil physics. Base exchange is certainly one of the fundamental properties of soils, and the clay minerals play an important part in base exchange. But, despite the extensive study on base exchange, much remains to be determined. As Dr. Grim and others have pointed out, there is good reason for the belief that the crystal structure of the clays, together with the specific nature of the positive ions of the tetrahedral layers and possibly of the octahedral layers of the lattice, largely determines base exchange and possibly the physical properties of the clays as well. However, it should be kept in mind that this view is as yet largely hypothetical. It needs further proof.

All the aforementioned physical and chemical properties of soils are probably largely determined by the specific properties of the clay minerals present. It is certainly no longer tenable to attribute base exchange in soils or the physical properties of the system to amorphous clay substances. In all probability both the physical and the chemical properties of soils are largely determined by the electrical forces that are active on the surface of clay crystals. Soil physics and soil chemistry are, therefore, manifestations of the physics and chemistry of surfaces. Soil science will profit greatly by the elucidation of the forces that are active on the surfaces of the crystals of the different types of clay minerals.

SOIL SCIENCE AND GEOLOGY

Modern researches on the clays are therefore placing the subject of soils on a new footing. They have served to emphasize the close relationship between soil science and geology and mineralogy. This is particularly important for the reason that during the last thirty or forty years certain influential soil workers have attempted to draw a sharp line between soil processes and geological processes. Soil is defined by this school as a natural body largely independent of geology. Weathering of the undecomposed mineral fragments in soils is looked upon as the continuation of geological weathering, but not as a soil process. The leaching-out of soluble salts, formed in soils by the hydrolytic action of rain waters charged with more or less carbon dioxide, is likewise considered a geological process. The chemical processes taking place in soils are thus largely cast aside as of but little, if any, pedological importance. According to this view, clay formation belongs to geology. Hence, those soil workers who hold this view take but scant interest in clay-minerals researches. Erosion is likewise disposed of as being either artificial or purely geological.

In my opinion these notions are wholly untenable. The disintegration and chemical weathering of igneous, metamorphic, and sedimentary rocks, leading to the formation of soils containing more or less clay and capable of producing various kinds of crops, is a continuous process. As the weathering progresses, the rates of these processes undoubtedly tend to slow down, but as long as the materials are exposed to weathering agencies these processes never come to an end. There simply is no point where you can separate geological from soil processes.

That clay research is drawing soil science into closer contact with geology is one of its important by-products. In my opinion the closer the co-operation between soil workers and geologists, the better. In fact, I look upon several of the important phases of soil science as aspects of geology. Soils are obviously the superficial, unconsolidated materials on or near the surface of the earth. At some later period in geological history, the materials now present as soils will become sandstones, shales, clay deposits, or something else, just as

the materials now composing the shale deposits were derived from products of weathering of a previous age, much of which was probably soil material at some previous time. There simply is no dividing line between soil science and geology.

A considerable number of soil scientists have already been greatly stimulated by the clay researches, and this stimulation is destined to extend into future years. Nevertheless, these researches have not as yet very greatly affected practical agriculture. It is almost certain, however, that practical applications will be found when the properties of the clays are better understood and particularly when soil scientists have more fully explored the subject.

APPLICATIONS OF MODERN CLAY RESEARCH IN CERAMICS[1]

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ABSTRACT

There are given here some modern ideas concerning the nature of clay, which is shown to be a very complex material whose physical properties are greatly influenced by such variables as adsorbed ions, organic matter, particle size, and many others.

INTRODUCTION

From prehistoric times clay has been recognized as a particularly suitable material with which to form vessels, both utilitarian and decorative. The reason for this is not at all hard to find, for clay possesses the property of plasticity, which allows it to be readily formed by hand or on the potter's wheel to the desired shape. Further than this, the clay dries with sufficient strength to permit handling, and, last, it can be fired into a more or less hard and durable article.

Natural clay occurs with greatly varying properties, some being highly plastic, some sandy, some light, and some dark. The potter has found by trial-and-error method that certain clays or certain combinations of clays were suited to their particular needs. It is only comparatively recently that we have been able to show that clays are largely composed of definite minerals with a small amount of organic matter. Now we can literally take a clay apart and classify all its components and from this build a scientific method of selecting and preparing clays.

In ceramics, clay may be used as a stiff plastic mass or as a slip thin enough to pour. As it is best to treat these two consistencies separately, the plastic masses will be first considered.

THE CLAY-WATER SYSTEM

PLASTICITY

The term "plasticity," which is always associated with mixtures of clay and water, is difficult to define and still more difficult to meas-

[1] Address delivered at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941.

ure. To the rheologist, plasticity means the property of matter which permits it to be deformed, the deformation remaining after the deforming force is removed. In more practical terms, we speak of a mass as having workability when two conditions are satisfied. In the first place, it must have a sufficiently high yield point, so that the formed piece will not deform under the forces of gravity or the shocks of handling, and, in the second place, the mass must be deformable to a large degree without showing rupture. In other words, the clay-water masses used in ceramics are of the elastico-plastic

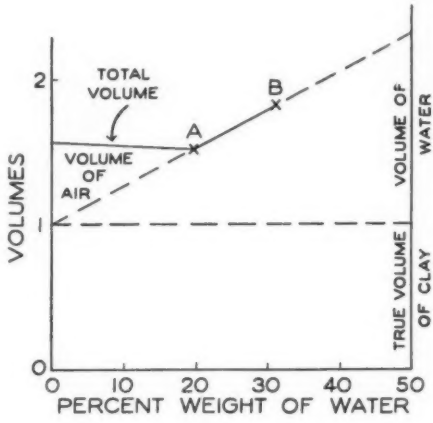


FIG. 1

type, as a finite force is needed to initiate flow, and, after the flow starts, the deformation is plastic. Except for the smaller forces employed, the clay-water masses have the same flow properties as soft metals.

PLASTIC MASSES

It is perhaps most logical to illustrate the clay-water system by the diagram of Figure 1, where the volumes of clay, water, and air are plotted as ordinates and the amount of water in the system as abscissa. Starting at the left-hand side of the diagram, it will be seen that the volume of clay remains constant, but the water increases as a straight-line function. The total volume expressed by

the upper line in the diagram will, of course, include the air which, at the low-water contents, is a component of the system. However, as the water is increased, the pores between the clay particles are gradually filled, thus displacing the air, until as point *A* is reached what is called the "saturation point," where there is a two-component system, clay and water. At this point the mass changes from a damp powder to a homogeneous plastic mass. In most cases additional water can be added up to the point *B* before the excess is forced out of the mass at the low-molding pressure illustrated in this diagram.

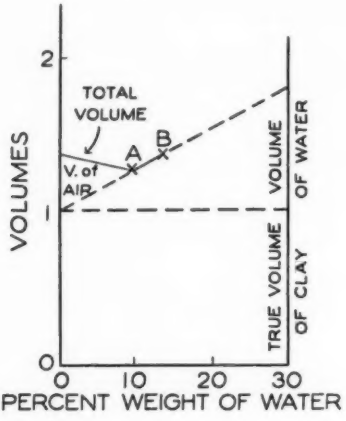


FIG. 2

Therefore, the range between *A* and *B* is the working range of the mass.

In Figure 2 there is shown a similar diagram under conditions of very high-forming pressures. Here the volume of clay is the same as before, but the total volume is less, owing to the greater compacting of the mass, and for that reason less water is needed to reach the saturation point *A*. Here again additional water can be added up to point *B* before it is squeezed out of the mass.

These diagrams are more or less idealized and would vary to some extent with different clays, particularly with changes in size distribution. For example, a clay containing principally one size of

particle would have a relatively high porosity, and the bulk volume would be large, whereas another clay might have a distribution of particles to give a close packing, in which case the amount of water needed to reach point *A* would be considerably less. The same is true in ceramic bodies where nonplastic materials are added to the clay and give a closer packing.

CASTING SLIPS

If the amount of water in the system is increased to perhaps 100 per cent of the weight of clay, a fluid slip will be obtained which can be poured and will form accurate casts in intricate molds. Such a large amount of water, however, is a disadvantage in that the shrinkage of the clay is very high and the drying is difficult. Therefore, it has been found that the addition of certain chemicals, which are usually monovalent salts giving an alkaline reaction, make it possible to obtain the desired fluidity with much less water, perhaps as low as 25 or 30 per cent, with a corresponding increase of specific gravity. Here again the properties of the slip are greatly dependent on the characteristics of the clay, and really satisfactory slips can be made up only with a very carefully blended mixture of clays and nonplastics.

DRYING CHARACTERISTICS

When the molded or cast piece is dried, shrinkage occurs, owing to the elimination of the thin water films between the clay particles. The maximum stable thickness of these water films is not more than 0.01 μ, and it is quite obvious that the finer the grain of clay the greater the number of these films that will occur within a given distance and, therefore, the greater the shrinkage. Consequently, it is obvious that fine-grained clays will have a much greater shrinkage than coarse-grained clays. The drying shrinkage of the clay is of practical interest because it influences the warping and cracking of the clay. A low shrinkage is highly desirable and can be obtained by proper sizing of the ingredients and the introduction of nonplastic material, which simply acts as a replacement for some of the shrinking clay.

It should be noted that, as far as we can tell, it is impossible to produce plasticity in a clay-water system without having water films

surrounding the clay particles. These films act as a lubricant and adhesive to give the extensibility and the yield point needed for working the mass. Therefore, on drying, these films are removed, and the clay will shrink.

In Figure 3 is shown a typical drying-shrinkage curve of a clay. It will be noted that down to point *A* the volume of water removed is exactly equal to the volume loss of the piece, showing that air does not enter the system. Beyond point *A*, however, the volume

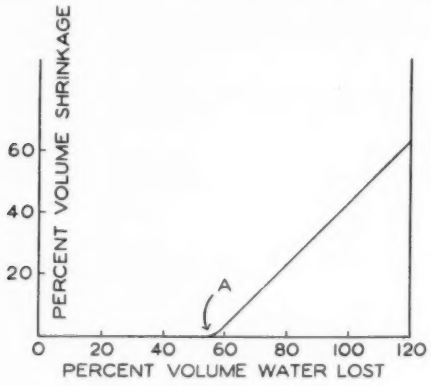


FIG. 3

loss more or less suddenly stops simply because the clay particles are touching each other, and from there on the water removed is from the pores and is replaced by air.

CERAMIC MOLDING METHODS

DRY PRESSING

Many types of ceramic articles are manufactured by the dry-press or dust-press method. This includes refractories, electrical porcelains, and many other products. In this method of molding the clay or clay and nonplastic material is mixed with a comparatively small amount of water, perhaps 6 or 10 per cent, which forms a comparatively dry-appearing powder. This material is then formed under high pressure, perhaps as high as 5,000–10,000 pounds per square

inch in steel dies, under which conditions it is compacted into a strong coherent mass which has no air shrinkage, because insufficient water has been supplied to form films between the particles.

EXTRUSION MOLDING

Under these conditions the clay is made up with sufficient water to bring it up to point *A* in Figure 1, perhaps 20–25 per cent. It is a plastic mass, but one which is so stiff that considerable force is necessary to form it. This mass is then extruded in various ways through a die to form a uniform column of any desired shape, which can be cut off with a wire at unit lengths. Here there is a small amount of drying shrinkage, as water films have been built up between particles to some extent.

PLASTIC MOLDING

In this type of molding the clay has even more water added (25–30 per cent), approaching point *B* in Figure 1. This gives a mass having the consistency of molding clay which can be readily deformed but which still has a sufficient yield point to prevent gravity forces from deforming it on standing. The mass is formed in any number of methods, such as throwing on the potter's wheel or forcing into a brick die. In this case the drying shrinkage of the mass is considerable, because the water films are comparatively thick.

CASTING PROCESS

In this process the slip is made up of clay and water and a deflocculant to a pouring consistency and is then placed in plaster of paris molds and allowed to remain until a wall of the desired thickness is cast out on the inner surface of the plaster mold. The remaining slip is then drained, leaving the hollow vessel in the plaster mold. In some cases solid castings are made, the slip being left in the mold long enough to produce a solid piece. Here again, there is considerable drying shrinkage, because the water films that are built up have considerable thickness. The casting process is particularly adaptable to thin-walled ware such as porcelain, but it can also be used for heavier ware, like certain types of refractory, where a large amount of nonplastic material is incorporated in the slip.

CLAYS AND THEIR TREATMENT

TYPES OF CLAY

There are a great many types of clay, and they are often classified as to their use; for example, the china clays, which are exceptionally pure and white burning for use in pottery and china, and the ball clays, which are comparatively white burning but are very fine grained and highly plastic. There are refractory clays which are used for making firebrick, stoneware clays for making stoneware, and many other classifications too numerous to mention here.

The geologist also classifies clays as to their origin, such as the residual clays which are found in the position of the parent-rock from which they were derived by weathering or the sedimentary clays which are transported and laid down in new beds with more or less alteration during the process.

CLAY MINERALS

There was formerly a great deal of speculation as to the nature of clay, many considering clays made up of more or less colloidal material. Modern methods of analysis, however, such as the X-ray and the thermal analysis apparatus, have enabled us to determine that clays even in the finest fractions are crystalline plates of specific minerals. A number of these clay minerals have been definitely established, but there are probably others which will be determined in the future in spite of the great difficulty in working with such fine-grained materials. It is sufficient to say that here practically all the clays of interest to the ceramist are composed of the mineral kaolinite in various sizes. The most frequent size runs from 0.2 to 0.8 μ, as shown by the curves in Figure 4.

ACCESSORY MINERALS

Nearly all the natural clays contain so-called "accessory minerals," which are really impurities in the clay itself. These consist of quartz, mica, the iron minerals, and many others in smaller amounts. These accessory minerals in some cases do no harm, as when the clay is used as building units or refractories. On the other hand, if the clay is to be used for fine tableware, then it is necessary to remove as much as possible of these nonclay minerals.

WASHING

This is carried out in general by a water washing of the clay, which floats off the finer kaolin plates and allows the quartz, mica, and other undesirable minerals to settle. This washing is accomplished in a number of different ways, but often by allowing a diluted slip of the raw clay to flow down long troughs containing riffles, which allow the coarser minerals to settle. In more modern installations the accessory minerals can be removed by a high-speed continuous centrifuge.

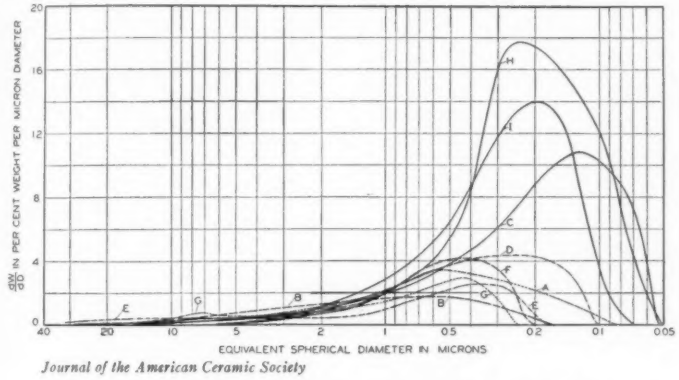


FIG. 4.—Size-distribution curves for a number of ceramic clays

CHEMICAL TREATMENT

In a few cases clay is chemically treated to remove some of the iron which acts as a colorant and gives the clay a creamy tinge. This chemical treatment is used most generally for paper clays rather than for ceramic clays, as the bleaching operation takes out surface iron rather than iron in the interior of the particle. One of the most common methods of bleaching is to treat the clay slip with zinc hyposulphite.

PARTICLE-SIZE CONTROL

As will be shown later, the particle-size distribution in the clay is of great importance in its subsequent use, and, therefore, some of the more progressive companies are now producing clay which has been classified as to grain size either by settling methods or by passing

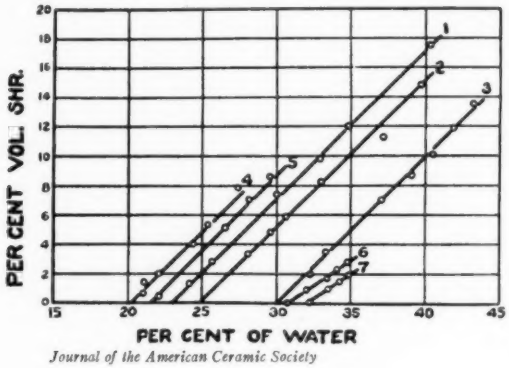
through a continuous centrifuge. By these methods it is quite possible to produce a clay with a reproducible size distribution.

VARIABLES IN CLAY THAT INFLUENCE THE MOLDING PROPERTIES

There are a considerable number of variables in clay which have a profound influence on the molding properties when used in the ceramic industry. It is proposed to discuss these variables in some detail and show how they influence the working properties.

PARTICLE SIZE

As shown previously, the plastic properties and the drying shrinkage are quite dependent on the particle size. This can perhaps be



Journal of the American Ceramic Society

FIG. 5

more clearly shown in Figure 5, where there is plotted the drying shrinkage for a series of clays of different average particle size. It will also be found that the plastic properties vary with the particle size, the plasticity decreasing as the average size becomes larger. Also, the properties of the casting slip will be greatly dependent on this factor. Natural clays, even with careful control, vary somewhat in particle size from one portion of the bed to another, and, therefore, the consumer sometimes finds difficulty in keeping a constant product because of this variable.

TYPES OF CLAY MINERAL

It was stated in the previous section that most of the commercial clays used in ceramics contained the mineral kaolinite, but certain types of clay, such as the ball clays, may contain a small proportion of other clay minerals, such as montmorillonite. This mineral is very fine grained, swells in the presence of water, and in general gives to the clay mass an increased plasticity. Therefore, a variable amount of this mineral in the clay may materially alter the plasticity and drying properties of the clay.

SOLUBLE SALTS AND ADSORBED IONS

Nearly all the natural clays contain soluble salts from the percolating ground water and also adsorbed material on the surface of the clay, such as calcium and potassium. These adsorbed materials are of particular interest to the soil chemist, as they are the basis of plant growth, but they are also of interest to the ceramist because they profoundly influence the properties of the clay-water system in which they are used. Perhaps the variation in adsorbed ions from time to time gives the ceramist more trouble than any other variable, particularly in the making-up of casting slip because of the interference with the deflocculating agent.

PARTICLE SHAPE

It is difficult to determine accurately the shape of the finer clay particles, but we believe them to be always platelike, and there is good reason to believe that some clays have thinner plates than others. This variation in shape undoubtedly has an influence on the properties of the clay in the wet condition. Much more study with the electron microscope will be necessary in this connection to determine this factor precisely.

ORGANIC MATTER

Nearly all clays contain some organic matter, such as lignite or humic acid, which have an important influence on the plasticity of the clay. For example, the ball clays contain a considerable amount of organic matter, which is believed to be one reason for their high plasticity. The coarser types of organic matter can be screened out of the clay, but the finer can be removed only by rather complicated chemical processes.

CONTROL OF THE CLAY VARIABLES IN CLAY PROCESSES

In the future the manufacturer of ceramics is going to demand a tailor-made clay which has all the variables mentioned in the previous section under a reasonable degree of control. While at the present time it is not feasible to produce clay in large quantities, with an exact control of the properties this can be done quite readily in the laboratory. For example, the grain size can be readily controlled by settling or centrifuging from a dilute suspension, the organic matter can be removed by an oxidizing treatment with hydrogen peroxide, and the soluble salts and adsorbed ions can be removed by leaching with an acid or by electrodialysis. If these steps have been carefully taken, a clay can be produced of definite grain size, definite mineral content, a definite amount of adsorbed ions, and with controlled organic matter. It is this type of clay which will be more and more in demand by the manufacturer in the next few years.

REVIEWS

The Last Million Years: A History of the Pleistocene in North America.[1] By A. P. COLEMAN. Edited by GEORGE F. KAY. Toronto: University of Toronto Press, 1941. Pp. xii+216; figs. 56. $3.50.

In this attractive posthumous volume there is presented, in pleasing form, a summary statement by the late Dr. A. P. Coleman of the results of his own studies of the glacial and associated deposits of North America, together with well-chosen references to many papers of his contemporaries. His field studies in North America were mostly in Canada, and he has endeavored to show to what extent the Canadian phenomena fit in with the interpretations of multiple glaciations by the glacial geologists in the states to the south of Canada. How the smaller number of glacial beds found in many places is to be fitted into the typical classification as worked out in the Mississippi Valley is, as stated, "sometimes hard to decide and it is probable that important parts of the glaciated country were not covered by the full number of ice sheets" (p. 46).

One of Professor Coleman's conclusions is expressed in part as follows:

> The rude work of the glacier has attracted more than a fair share of attention and the evidence of interglacial stages has often been overlooked entirely. The present work has been written largely to restore the balance and to show how important and how extensive the interglacial periods have been in the history of the Pleistocene [p. 203].

Some of the fossiliferous beds, which have been regarded as of post-Wisconsin age, he thought probably represent earlier stages of deglaciation. He also writes: "I am now inclined . . . . to suggest that during the Pleistocene much more time was warm than cold, so that the name Ice Age often applied to it is not entirely appropriate."

While calling particular attention to the evidence as to climatic conditions furnished by Pleistocene faunas and floras, he did not in general minimize the effects of the ice invasions themselves, and he has introduced some very interesting word pictures of conditions attending the waxing and waning of the great ice sheets. Of the last or Wisconsin stage of glaciation he says:

> The usual idea that the Wisconsin ice covered all of eastern America north of New York and nearly reached the earlier limits of glaciation can no longer be

[1] Review published with the permission of the director of the Geological Survey, U.S. Department of the Interior.

sustained. In Labrador and Newfoundland, as well as south of the Gulf of St. Lawrence, there were large valley glaciers and perhaps local ice caps but there was no continuous sheet of ice [p. 120].

Concerning this the editor, Dr. George F. Kay, a prominent glacial geologist and a former student of Professor Coleman, states in a note, "Several well-known Pleistocene geologists who have done field work in recent years in one or more of the areas discussed in this chapter have reached interpretations differing from those held by the author" (p. 121).

From his own observations on numerous peaks in British Columbia, and those of other geologists, Professor Coleman concluded that "there can be no doubt that the Cordilleran ice sheet filled the whole mountain region of British Columbia and left its marks at 7,000 or 8,000 feet on all projecting summits" (p. 140). However, he states, "it appears that the lower part of the ice, hemmed in between the mountains, remained stagnant for thousands of years" (p. 140).

After citing briefly such evidence of the presence of man in the Pleistocene, as has been found, he states that "it should not be surprising to find evidence of man in America at any time after his appearance in the Old World" (p. 194).

In chapter xi Dr. Coleman discusses the duration and the causes of ice ages. In making one time estimate himself, he started with the rate at which the cliffs were receding where attacked by the waves of Lake Ontario, and, making allowance for various factors, he reached a conclusion that "this would make the whole time since the ice began to leave the Ontario basin, and Niagara Falls commenced its work, 24,000 years" (p. 201). But, he states, "the age of Niagara has been variously estimated at from 7,000 to 50,000 years, and as a chronometer it has proved a disappointment because of the unexpected complications entering into its history" (p. 200). He also gives some time estimates made by other geologists based on various factors, such as the weathering of the several drift sheets and the number of annual layers of clay (or varves) deposited in glacial lakes.

As to the causes of ice ages, he states:

> It is safe to say that the more cautious and experienced students of the Pleistocene find its repeated and striking changes very difficult of explanation. Each theory taken by itself breaks down at some point and fails to cover all the phenomena of the baffling geological period of the last million years [p. 206].

Viewing the future of the human race, he concludes: "We may expect that thousands of generations will pass away before the polar regions lose

their ice sheets and civilization has to migrate to the far north and the far south to find an endurable climate" (p. 210).

On the whole, the book will be interesting and valuable for both laymen and geologists. Possibly some of the latter might have preferred that the editor had omitted the proposed revised classification of the Pleistocene of the Mississippi Valley from chapter iii, inasmuch as it appears to have been inserted since Dr. Coleman's death and there is no indication as to his opinion of it. It may also be noted in passing that some geologists do not see the need of introducing four new "epoch" names as subdivisions of the Pleistocene, the whole of which they prefer to consider an *epoch* rather than a *period*, as compared in length with the Tertiary and earlier geologic periods.

WILLIAM C. ALDEN

The Structure of the Kejser Franz Josephs Fjord Region, North-East Greenland. By N. E. ODELL. ("Meddelelser om Grønland," Band 119, No. 6.) Copenhagen: C. A. Reitzels Forlag, 1939. Pp. 54; figs. 22; pls. 6. Kr. 2.50.

Pioneer studies have shown that the geology of northeast Greenland is by no means simple. While its broader outlines are becoming apparent, there have arisen important questions of interpretation and considerable differences of opinion. With these in mind the author, a member of the Louise A. Boyd Expedition of 1933, visited certain districts for crucial evidence which would help answer a few of these questions. The additional information obtained in the short time available is presented and critically discussed in this report.

Exposed between the inland ice and the eastern coast is a north-south belt of metamorphic complex with strips of less metamorphosed pre-Devonian sediments of great thickness on either side. Nearer the sea are Devonian sandstones and conglomerates and some Carboniferous beds. Odell does not subscribe to the view that the rocks of the complex owe their metamorphic condition mainly to granitic intrusions at the time of the Caledonian folding. Instead he favors the view that dynamic metamorphism has been predominant and that some of it probably dates from the pre-Cambrian. He recognizes older granites and younger granites. On the other hand, he believes that the Caledonian deformation extended much farther west than has generally been supposed, because he found the Petermann series (considered the western equivalent of the eastern Eleonore Bay formation) to be abruptly overfolded. But although granite

and some basic sheet intrusions accompanied the Caledonian folding, these were not responsible for more than local metamorphism.

Further contributions have been made to the later history of the east coast. There is evidence of what may prove to be a Hercynian disturbance, although the time relations of this are as yet rather vaguely established. Extensive block faulting occurred early in the Tertiary, followed by volcanic activity on a grand scale.

The reviewer has long wondered why there should be this east-coast Caledonian range extending south at a right angle from the main Caledonian folding which runs westward from Spitzbergen along the north side of Greenland and the northern border of the North American continent. The present report, of course, covers only a relatively small area, but the reviewer gathers the impression that the north-south trending folds become notably less pronounced to the north in the direction of the main east-west chain; they appear to be more conspicuous south of latitude 73°. One may therefore ask: Will the evidence permit entertaining the hypothesis that the north-south folding of eastern Greenland belongs with the Acadian orogeny of New England and eastern Canada (with which it is more or less in line) rather than with the Caledonian orogeny (*sensu stricto*) so well understood in Europe? The latter occurred near the close of the Silurian, giving rise to the Old Red sandstone from early to late Devonian time; the former commenced in mid-Devonian times starting the thick Hamilton shales and developing the reddish Catskill facies of later Devonian age as the orogeny came to a climax. One notes that in eastern Greenland some of the Devonian was involved in the folding, although this fact need have no decisive bearing on the question until the ages of the Devonian formations of eastern Greenland can be more precisely determined. In any case the geologic problems of this region are of much more than local importance.

R. T. C.

The Geology and Ore Deposits of Northeastern New Mexico. By GEORGE TOWNSEND HARLEY. (New Mexico School of Mines Bull. 15.) Socorro, N.M., 1940. Pp. 105; pls. 5; figs. 11. $0.60.

This report has been prepared particularly for the use and information of prospectors, owners, and operators of mining property. The first part describes the physiography and rock formations and gives a brief review of the geological history of the region. This is followed by a detailed description of the individual mining districts.

The ores have been derived from three sources. Gold and silver, and sulphides of zinc, lead, copper, and molybdenum, are found in the pre-Cambrian rocks, and the evidence indicates these ores were formed in pre-Cambrian time. The second class includes the copper deposits in Triassic sediments, which some think to be syngenetic with deposition of the sediments. A third, very minor, source is the Quaternary basalts, which contain limited stringers of gold. The Pecos Mine is an example of the first class of deposition and the Stauber orebody of the second. Aside from these two, which have been important producers, all known deposits are commercially unimportant.

C. W. STERNBERG

The Tertiary Foraminifera of Porto Rico. By J. J. GALLOWAY and CAROLINE E. HEMINGWAY. ("Scientific Survey of Porto Rico and the Virgin Islands," Vol. III, Part IV.) New York: New York Academy of Sciences, April, 1941. Pp. 275–491; pls. 36. $2.00.

This volume is an excellent aid to the student of Tertiary foraminifera. The assemblage represents twenty-five families, ninety-nine genera with 275 species and varieties, of which eighty-eight are new. The collection was made from six formations, probably ranging in age from the Middle Oligocene to the Lower Miocene. Data on depth distribution of the various families lead the authors to postulate accumulation at relatively shallow depths. A check list of the formations of the north and south shore, as well as one showing relative abundance and stratigraphic distribution of the foraminiferal faunas, are included.

The synonymy and descriptions are adequately done. The excellent plates are wash drawings reproduced by the collotype process.

ERNEST P. DU BOIS

CONSERVATION OF SCHOLARLY JOURNALS

The American Library Association created this past year the Committee on Aid to Libraries in War Areas, headed by John R. Russell, the librarian of the University of Rochester. The Committee is faced with numerous serious problems and hopes that American scholars and scientists will be of considerable aid in the solution of one of these problems.

One of the most difficult tasks in library reconstruction after the first World War was that of completing foreign institutional sets of American scholarly, scientific, and technical periodicals. The attempt to avoid a duplication of that situation is now the concern of the Committee.

Many sets of journals will be broken by the financial inability of the institutions to renew subscriptions. As far as possible they will be completed from a stock of periodicals being purchased by the Committee. Many more will have been broken through mail difficulties and loss of shipments, while still other sets will have disappeared in the destruction of libraries. The size of the eventual demand is impossible to estimate, but requests received by the Committee already give evidence that it will be enormous.

With an imminent paper shortage attempts are being made to collect old periodicals for pulp. Fearing this possible reduction in the already limited supply of scholarly and scientific journals, the Committee hopes to enlist the co-operation of subscribers to this *Journal* in preventing the sacrifice of this type of material to the pulp demand. It is scarcely necessary to mention the appreciation of foreign institutions and scholars for this activity.

Questions concerning the project or concerning the value of particular periodicals to the project should be directed to Wayne M. Hartwell, executive assistant to the Committee on Aid to Libraries in War Areas, Rush Rhees Library, University of Rochester, Rochester, New York.